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# Synthesis and structural characterization of $(\text{CH}_2)_n$ -bridged indenyl-pyrazoles and their cyclopentadienyl nickel(II) complexes

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## ABSTRACT

A new class of  $(\text{CH}_2)_n$ -bridged indenyl-pyrazoles [4-{Ind- $(\text{CH}_2)_n$ }-RR'PzH] (Ind = 1*H*-inden-3-yl,  $n = 1-3$ , RR'Pz = 3,5-disubstituted pyrazolato) were synthesized. Reactions of the indenyl-functionalized pyrazoles with nickelocene in refluxing toluene afforded trimetallic and dimetallic cyclopentadienyl nickel(II) complexes, i.e.,  $[\text{CpNi}\{4\text{-}(\text{Ind-}(\text{CH}_2)_n\text{-RR'Pz})_2\}_2\text{Ni}]$  and  $[\text{CpNi}\{4\text{-}(\text{Ind-}(\text{CH}_2)_n\text{-RR'Pz})\}_2]$ , depending on the steric hindrance from the 3,5-disubstituents on the pyrazolato rings. In the CpNi(II) complexes, pyrazolato ligands exhibit  $\mu\text{-}\eta^1$  coordination to the metal centers and the indenyl moieties demonstrate no interaction with the metals. All the indenyl-pyrazoles and their complexes were characterized by spectroscopic and analytical methods including X-ray crystallographic study.

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## 1. Introduction

Pyrazolato ligands have demonstrated rich coordination chemistry due to their diverse coordination modes to metals [1–11]. Pyrazoles and pyrazolato ligands are potentially useful in design of transition metal complex catalysts [12] and construction of metal architectures [13]. Metal complexes of side chain-functionalized cyclopentadienyl ligands have been paid considerable attention over the past decade. *ansa*-Carbon-bridged cyclopentadienyl ligands have been well documented due to the dramatic effect of an incorporated *ansa*-bridge on the stability of their transition metal and lanthanide complexes [14–16]. *N*-Donor side chain-functionalized indenyl ligands of type **A** (Chart 1) have also been paid attention in coordination chemistry. *ansa*-Bridged indenylamido complexes of titanium and niobium [17] and  $\text{CH}_2$ -bridged pyrrolyl-indenyl complexes of lanthanides Sm, Yb and Eu [16] were reported.  $\text{NR}_2$ -containing side chain-functionalized indenyl complexes of lanthanides Yb and Eu have demonstrated novel chemistry [18–20]. *N*-Heterocyclic carbene (NHC)- $(\text{CH}_2)_n$ -functionalized indenyl complexes of transition metals Ti, Zr, V, and Cr [21], and Ni [22], and lanthanide Y [21] have recently been documented. NHC- $(\text{CH}_2)_n$ -functionalized fluorenyl complexes of metals have also been known [21]. Nitrogen or other heteroatom-donor side chain-functionalized pyrazolates can serve as polydentate ligands, and a pyrazol-1-yl tethered to a Cp ligand might also serve as an intramolecular function as a chelate donor in metal complexes

[23–26]. Bis(cyclopentadienyl)-functionalized pyrazoles (**H<sub>3</sub>L**), i.e., 3,5-bis(fluoren-9-ylmethyl)-1*H*-pyrazole and 3,5-bis(inden-3-ylmethyl)-1*H*-pyrazole, and their lithium salts (**Li<sub>3</sub>L**) were synthesized [27] (Chart 1). In the above-mentioned *N*-donor side chain-functionalized cyclopentadienyl (or indenyl and fluorenyl) complexes, the cyclopentadienyl ligand exhibits or does not demonstrate coordination to the metal center.

Pyrazoles have exhibited versatile reactivity to organometallic compounds, forming a wide range of pyrazolato complexes [1–12]. The reactions of nickelocene with 4-*X*-3,5-dimethylpyrazole ( $X = \text{H}, \text{Cl}, \text{Br}, \text{CH}_3, \text{and NO}_2$ ) and 3,5-bis(perfluoromethyl)pyrazole) in benzene were reported to form dimetallic (at room temperature) and trimetallic (at elevated temperature) cyclopentadienyl nickel(II) pyrazolato complexes, i.e.,  $[\text{CpNi}(4\text{-}X\text{-}3,5\text{-RR'Pz})_2]_2\text{Ni}$  and  $[\text{CpNi}(4\text{-}X\text{-}3,5\text{-RR'Pz})_2]$  [28]. The direct reactions of nickelocene or manganocene with molten pyrazoles formed polymeric metal pyrazolates  $[\text{M}(4\text{-XPz})_2]_x$  ( $M = \text{Ni}, \text{Mn}$ ;  $X = \text{H}, \text{Cl}, \text{Br}, \text{or CH}_3$ ; Pz = pyrazolato or 3,5-dimethylpyrazolato) [29]. Formation of  $[\text{CpNi}(3,5\text{-RR'Pz})_2]$  from the reactions of  $\text{Cp}_2\text{Ni}$  and 3,5-disubstituted pyrazoles were also investigated by proton NMR techniques in an early report [30]. Although a variety of bridged cyclopentadienyl ligands have been developed and the emerging importance of replacing cyclopentadienyl groups with their heterocyclic analogues such as  $\eta^5$ -pyrazolato moieties has been aroused interest [9–11], a few reports have been reported on organometallic complexes bearing bridged indenyl-pyrazolato ligands [24,25,27]. During our ongoing investigation on pyrazole and pyrazolato chemistry [31–34], we have become interested in understanding whether the bridged indenyl-pyrazolato ligands display the same

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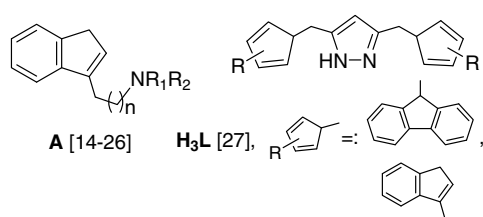


Chart 1.

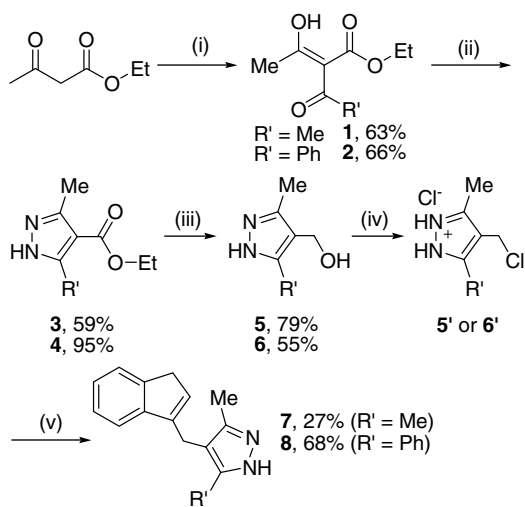
diversity in coordination chemistry as that of the non-functionalized pyrazolato ligands to late transition metals. Herein, we wish to describe synthesis and structural characterization of a new class of  $(\text{CH}_2)_n$ -bridged indenyl-pyrazoles and their trimetallic and dimetallic cyclopentadienyl nickel(II) pyrazolato complexes.

## 2. Results and discussion

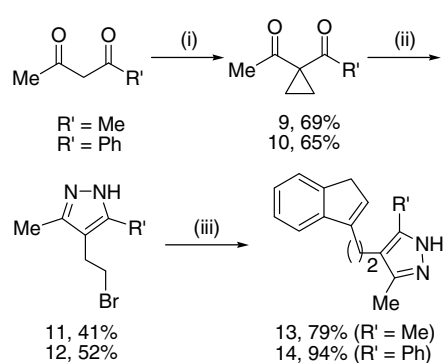
### 2.1. Synthesis of $(\text{CH}_2)_n$ -bridged indenyl-pyrazoles

$(\text{CH}_2)_n$ -Bridged indenyl-pyrazoles **7** and **8** were prepared by means of a modified five-step procedure [35] (Scheme 1). The ring closure reactions of ethyl 2-benzoyl-3-hydroxy-2-butenate (**1**) and ethyl 2-acetyl-3-hydroxy-2-butenate (**2**) with hydrazine dihydrochloride afforded pyrazoles **3** and **4** in 59% and 95% yields, respectively. Reduction of **3** and **4** with lithium aluminum hydride in diethyl ether at ambient temperature afforded 4-carbinols **5** and **6** which were transformed to 4-chloromethylpyrazole hydrochlorides **5'** and **6'** with thionyl chloride [36], respectively. The crude hydrochlorides were directly used for the next-step preparation. Thus, treatment of **5'** and **6'** with indenyllithium afforded pyrazoles [4-(Ind- $\text{CH}_2$ )-RR'PzH] (Ind = 1*H*-inden-3-yl; **7**: RR' = 3,5-dimethyl; and **8**: RR' = 3-methyl-5-phenyl). Pyrazole derivatives **11** and **12** were generated from the ring-opening reactions of intermediates **9** and **10** [37] with hydrazine hydrate in an aqueous  $\text{NH}_4\text{Br}$  solution [38]. Reactions of **11** or **12** with excess of indenyllithium produced  $(\text{CH}_2)_2$ -bridged indenyl-pyrazoles **13** or **14** in 79–94% yields (Scheme 2).

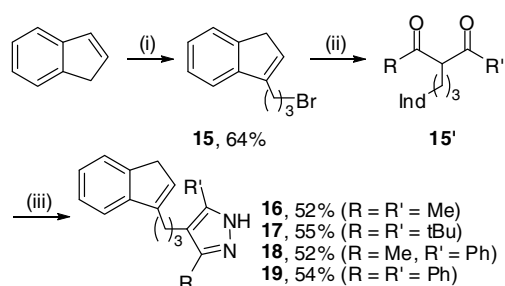
Alkylation of a  $\beta$ -diketone with (3-bromopropyl)indene (**15**) [39] in the presence of a base formed indenyl-functionalized  $\beta$ -diketone **15'** which was then reacted with hydrazine to afford 4-



**Scheme 1.** Synthesis of  $\text{CH}_2$ -bridged indenyl-pyrazoles **7** and **8**. Conditions: (i) Mg, EtOH,  $\text{CCl}_4$ , toluene,  $\text{CH}_3\text{COCl}$  (for **1**),  $\text{PhCOCl}$  (for **2**). (ii)  $\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$ , EtOH, r.t., 24 h. (iii)  $\text{LiAlH}_4$ , Et<sub>2</sub>O, r.t., 1 h. (iv)  $\text{SOCl}_2$ , 80 °C, 2 h. (v) Indene, KH, THF, r.t. to 60 °C.



**Scheme 2.** Synthesis of  $(\text{CH}_2)_2$ -bridged indenyl-pyrazoles **13** and **14**. Conditions: (i) 1,2-dibromoethane,  $\text{K}_2\text{CO}_3$ , DMSO, r.t., 12 h. (ii)  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ ,  $\text{NH}_4\text{Br}$  (aq. 10%), r.t., 24 h. (iii) Indene, *n*-BuLi, THF, r.t. to 60 °C.



**Scheme 3.** Synthesis of  $(\text{CH}_2)_3$ -Bridged Indenyl-Pyrazoles **16–19**. Conditions: (i) *n*-BuLi, THF, 1,3-dibromopropane, 0 °C to rt, 12 h. (ii)  $\text{K}_2\text{CO}_3$ , KI, acetone, reflux, 48–72 h. For **16**, acetylacetone; for **17**, 2,2,6,6-tetramethyl-3,5-heptanedione; for **18**, benzoylacetone; for **19**, dibenzoylmethane. (iii)  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ , EtOH, reflux, 2 h.

[Ind- $(\text{CH}_2)_2$ ]-substituted pyrazoles [4-{Ind- $(\text{CH}_2)_3$ }-RR'PzH] (**16**, RR' = 3,5-dimethyl; **17**, RR' = 3,5-di-*tert*-butyl; **18**, RR' = 3-methyl-5-phenyl; **19**, RR' = 3,5-diphenyl) in 52–55% yields (Scheme 3). All these indenyl-pyrazoles are soluble in organic solvents such as methylene dichloride, THF, chloroform, toluene and methanol. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR features in solution are in agreement with the proposed molecular structures of **7**, **8**, **13**, **14**, and **16–19**. The NH resonance signals of the indenyl-pyrazoles appear as broad peaks in the region 8.70–12.30 ppm, revealing presence of intermolecular hydrogen bonding between the pyrazole molecules. The characteristic NMR signals of Ind-CH are shown at 5.96–6.27 ppm, and the  $^{13}\text{C}$  resonance signals of the Pz-C4 are situated at 112.4–115.9 ppm. In addition, the molecular structure of **16** was further confirmed by X-ray single crystal structure determination (Fig. 1).

### 2.2. Synthesis of complexes **20–25**

Based on their preliminary studies, Blake and Storr suggested that, due to steric restraints, reactions of nickelocene with 4-*X*-3,5-dialkyl substituted pyrazoles (*X* = H, Cl, Br, Me, or  $\text{NO}_2$ ; alkyl = Me, or  $\text{CF}_3$ ) could yield dimeric  $[\text{CpNi}(\mu\text{-pz})_2]$  [28,30], trimetallic  $[\text{CpNi}(\mu\text{-pz})_2]_2\text{Ni}$  [28] or polymeric  $[\text{Ni}(\mu\text{-pz})_2]_x$  [29] complexes depending on the heating conditions. However, in our cases, reactions of nickelocene with **7**, **8**, **13**, **16** or **18** under mild (room temperature) or relatively harsh (in refluxing toluene) conditions only yielded trimetallic complexes of type  $[\text{CpNi}\{4\text{-(Ind-}(\text{CH}_2)_n\text{-RR'Pz})_2\}_2\text{Ni}$  (**20–24**) as red solids (38–84%) (Scheme 4), whereas the reaction of  $\text{Cp}_2\text{Ni}$  with indenyl-pyrazole **19** under the same conditions formed a dimeric complex, i.e.,  $[\text{CpNi}\{4\text{-(Ind-}(\text{CH}_2)_3\text{-3,5-Ph}_2\text{Pz})_2\}_2]$  (**25**) as red-purple solid (82%) (Scheme 5).

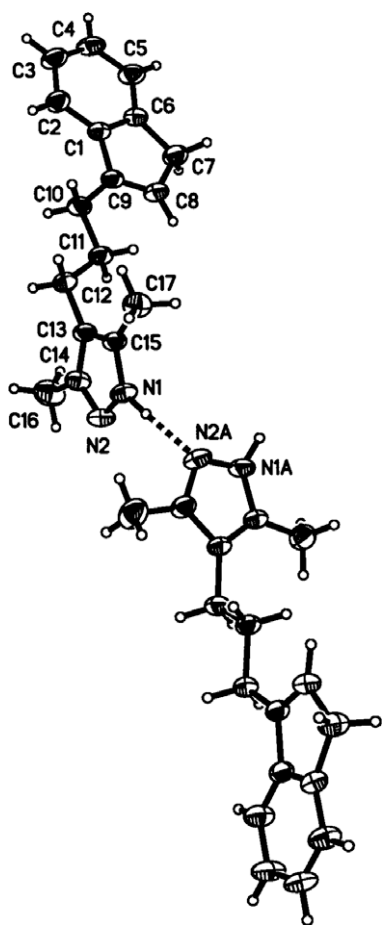
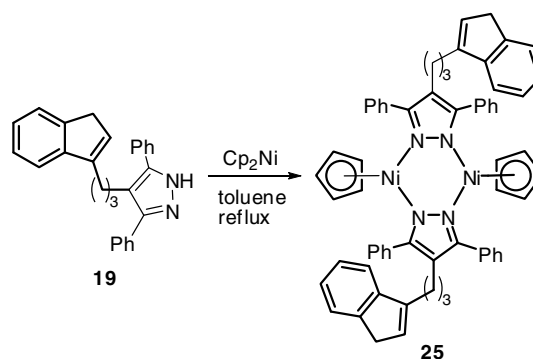


Fig. 1. Perspective view of compound 16.

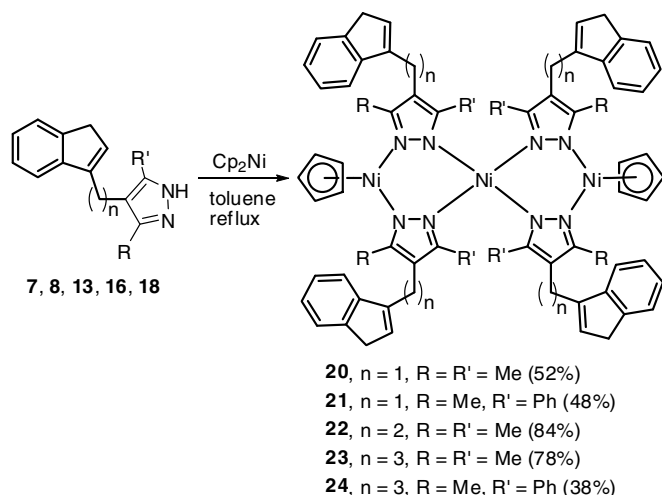


Scheme 5. Synthesis of dimetallic complex 25.

restraints from the indenyl and substituents on the pyrazolyl rings play a key role on formation of the tri- and dimetallic CpNi(II) complexes.

### 2.3. NMR spectral features

Complexes **20–25** are air- and moisture-stable at ambient temperature, and they demonstrate very similar NMR features in solution. Their  $^1\text{H}$  NMR spectra reveal presence of Cp and indenyl-pyrazolato ligands in 1:2 molar ratio in complexes **20–24**. The proton NMR signals of the Cp groups in **20–24** appear in the region of 4.30–5.63 ppm, and their corresponding  $^{13}\text{C}$  NMR signals are shown at 93–94 ppm. The steric hindrance from the substituents on the pyrazolyl rings has remarkable effect on the chemical shifts of the Cp protons. When the  $\text{RR}'$  groups are 3,5-dimethyl, the  $^1\text{H}$  resonance signals of the Cp rings in **20**, **22**, and **23** appear at 5.50–5.64 ppm, while the Cp proton NMR signals of **21** and **24** are shown at 4.24–4.30 ppm with  $\text{RR}' = 3\text{-methyl-5-phenyl}$ . When



Scheme 4. Synthesis of trimetallic complexes 20–24.

These results are attributed to the bulkier hindrance of the 3,5-diphenyl groups on the pyrazolyl ring of **19** than that of the Pz-3,5-disubstituents in other indenyl-pyrazoles. Attempt to prepare and isolate the desired product analogous to complexes **20–24** or **25** from the reaction of  $\text{Cp}_2\text{Ni}$  and **14** was unsuccessful. It should be noted that no reaction occurred between nickelocene and the bulkiest indenyl-pyrazole **17** in refluxing toluene (110 °C) or xylene (140 °C) over a period of 24 h. These results suggest that the steric

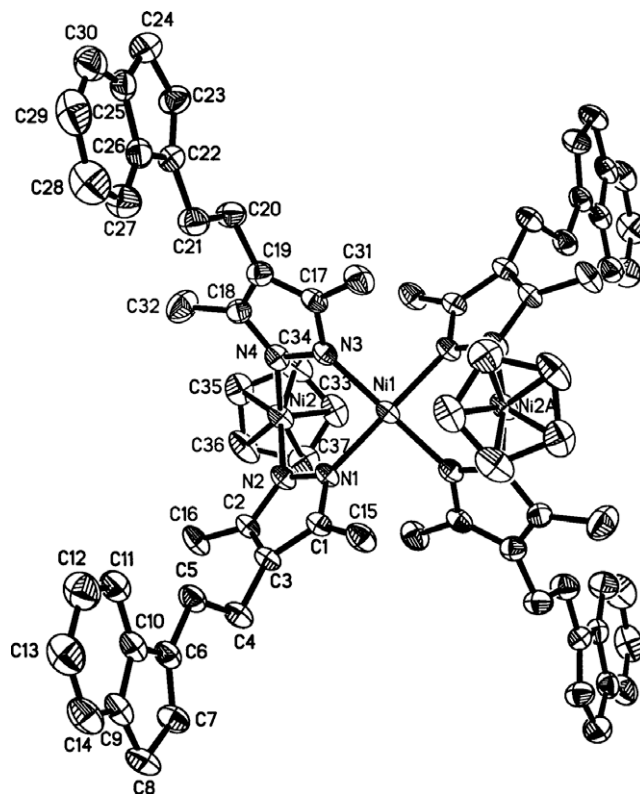


Fig. 2. Perspective view of complex 22.

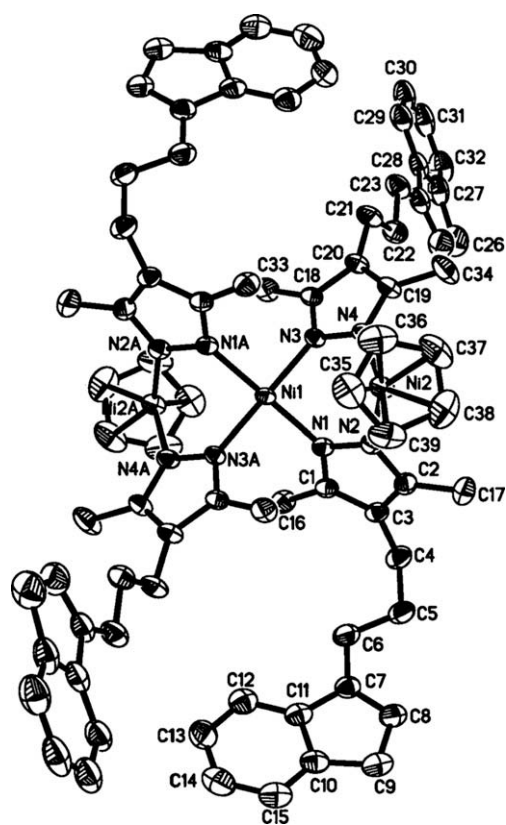


Fig. 3. Perspective view of complex 23.

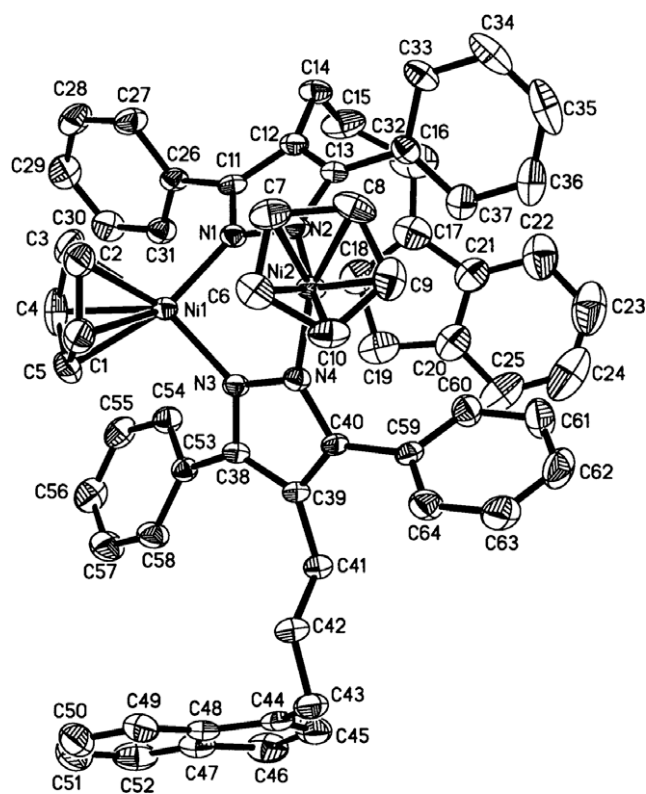


Fig. 4. Perspective view of complex 25.

the substituents are 3,5-diphenyl, the proton signals of the Cp groups in **25** are shown at 3.87 ppm. As compared with those of the free pyrazoles, the  $^{13}\text{C}$  NMR signals of the Pz-C4 are shifted downfield by 3–6 ppm, suggesting coordination of the pyrazolato systems to the metal centers. In the  $^1\text{H}$  NMR spectra of complex

**25**, the Cp and indenyl-pyrazolato ligands are present in 1:1 molar ratio, revealing a dimeric molecular structure. That the indenyl groups in complexes **20–25** are not bonded to the metal centers is included by the proton NMR signals of the indenyl-CH and  $\text{CH}_2$  protons which are nearly shown at the same positions as compared to those of the free indenyl-pyrazoles. The molecular struc-

**Table 1**  
Crystal data and refinement details for **16**, **22**, **23** and **25**.

	<b>16</b>	<b>22.2PhMe</b>	<b>23.2CH<sub>2</sub>Cl<sub>2</sub></b>	<b>25</b>
Empirical formula	$\text{C}_{17}\text{H}_{20}\text{N}_2$	$\text{C}_{88}\text{H}_{94}\text{N}_8\text{Ni}_3$	$\text{C}_{80}\text{H}_{90}\text{Cl}_4\text{N}_8\text{Ni}_3$	$\text{C}_{64}\text{H}_{56}\text{N}_4\text{Ni}_2$
Formula weight	252.35	1439.84	1841.53	998.55
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$
<i>a</i> (Å)	15.419(2)	10.7234(11)	10.9408(12)	13.3953(10)
<i>b</i> (Å)	5.2088(8)	11.7780(12)	12.8380(14)	12.3350(10)
<i>c</i> (Å)	18.805(3)	15.6336(16)	13.3883(15)	30.305(2)
$\alpha$ (°)	90	101.635(2)	87.034(2)	90
$\beta$ (°)	100.171(3)	102.674(2)	89.586(2)	98.569(2)
$\gamma$ (°)	90	96.320(2)	83.952(2)	90
<i>V</i> (Å <sup>3</sup> )	1486.6(4)	1862.1(3)	1867.5(4)	4951.4(7)
<i>Z</i>	4	1	1	4
<i>D</i> <sub>calc.</sub> (g cm <sup>-3</sup> )	1.128	1.284	1.317	1.340
$\mu$ (mm <sup>-1</sup> )	0.067	0.802	0.940	0.807
<i>F</i> (000)	544	762	778	2096
Crystal size (mm <sup>3</sup> )	0.50 × 0.43 × 0.33	0.44 × 0.28 × 0.06	0.49 × 0.47 × 0.10	0.47 × 0.41 × 0.20
$\theta$ limits (°)	1.58–25.99	1.37–27.00	1.52–26.00	1.79–27.00
No. of data collected	7647	11101	10220	28660
No. of unique data	2921	7928	7184	10791
[ <i>R</i> <sub>int</sub> ]	0.0785	0.0786	0.0853	0.0808
No. of data observed with [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1552	3293	4529	6777
No. of refined parameters	179	454	434	631
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	0.848	0.760	0.890	0.948
<i>R</i> (observed data/all data)	0.0507/0.0886	0.0542/0.1298	0.0547/0.0823	0.0556/0.0921
<i>wR</i> <sup>2</sup> (observed data/all data)	0.1190/0.1311	0.1057/0.1496	0.1237/0.1339	0.1205/0.1343
Residual $\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.162(–0.132)	0.437(–0.399)	0.633 (–0.562)	0.791 (–0.473)

tures of complexes **22**, **23**, and **25** were further determined by X-ray single crystal structural analysis (Figs. 2–4).

#### 2.4. X-ray crystal structures

The X-ray crystallographic data is summarized in Table 1 and bond distances listed in Table 2. Intermolecular hydrogen bonding is present between the molecules of indenyl-pyrazole **16** in the solid-state (N(1)–H(1)#1...N(2)#1, 1.96 Å, Fig. 1), which is also concluded by the solution NMR analysis. Complexes **22** and **23** exhibit trinuclear molecular structures that display a boat conformation for the six-membered Ni–(N–N)<sub>2</sub>–Ni ring systems in which the terminal nickel atom is coordinated by one cyclopentadienyl group, one anionic and one neutral pyrazolato N atoms, and the central nickel atom is coordinated by four pyrazolato N atoms with totally two anionic charges (Figs. 2 and 3). The terminal and central metal centers are bridged by two pyrazolato ligands demonstrating  $\mu$ - $\eta^1$ : $\eta^1$  coordination mode, and the indenyl groups show no interaction with the metal centers presumably due to the steric restraints from the substituents on the pyrazolyl rings. The cyclopentadienyl groups exhibit  $\eta^5$ -coordination to the terminal nickel atoms with Ni–C bond distances ranging from 2.074(5) to 2.167(5) Å (average 2.13 Å) in **22** and **23** (Table 2), and the two Cp groups are positioned *anti* to each other. The Ni–N distances are in the region 1.884(4)–1.912(3) Å, and the central nickel atom is linearly arranged with N(3) and N(3)#1, and also with N(1) and N(1)#1, that the angles N(1)–Ni(1)–N(1)#1 and N(3)–Ni(1)–N(3)#1 are 180° in **22** and **23** (Table 2). The molecular structure of **25** is depicted in Fig. 4. In contrast to complexes **22** and **23**, complex **25** exists in a dimeric form in which a boat conformation is also present for the six-membered Ni–(N–N)<sub>2</sub>–Ni ring systems with the two Cp groups arranged *syn* to each other. Each of the metal centers is coordinated by one  $\eta^5$ -cyclopentadienyl group and two pyrazolato nitrogen atoms. The average Ni–N distances of 1.908(2) Å in **25** is slightly longer than those (1.880(2) Å) in complexes **22** and **23**. There seems no obvious intramolecular sterical interactions that could cause such small difference, suggesting that intermolecular packing forces are responsible [28]. That the steric hindrance from the 3,5-diphenyl substituents on the pyrazolyl ring is bulkier than that of other 3,5-dialkyl or 3-alkyl-5-aryl substituents is attributed to the formation of different types of cyclopentadienyl nickel(II) complexes.

**Table 2**  
Selected bond lengths (Å) and angles (deg) for **16**, **22**, **23** and **25**.

Compound <b>16</b>	
N(1)–C(15)	1.345(2)
N(1)–N(2)	1.357(2)
N(2)–C(14)	1.329(2)
C(7)–C(8)	1.499(3)
C(8)–C(9)	1.327(3)
N(1)–H(1)...N(2)#1	1.96(2)
Complex <b>22</b>	
Ni(1)–N(1)	1.912(3)
Ni(1)–N(3)	1.884(4)
Ni(2)–N(2)	1.879(4)
Ni(2)–N(4)	1.881(4)
Ni(1)–N(3)#1	1.884(4)
Ni(1)–N(1)#1	1.912(4)
C(6)–C(7)	1.336(6)
C(7)–C(8)	1.514(7)
N(3)–Ni(1)–N(3)#1	180.00(1)
N(1)–Ni(1)–N(3)#1	91.03(16)
N(3)–Ni(1)–N(1)	88.97(15)
Complex <b>23</b>	
Ni(1)–N(1)	1.894(2)
Ni(1)–N(3)	1.894(2)
Ni(2)–N(2)	1.888(3)
Ni(2)–N(4)	1.887(2)
Ni(1)–N(3)#1	1.894(2)
Ni(1)–N(1)#1	1.894(3)
C(7)–C(8)	1.342(5)
C(8)–C(9)	1.491(5)
N(3)–Ni(1)–N(3)#1	180.00(10)
N(3)–Ni(1)–N(1)#1	90.59(11)
N(3)–Ni(1)–N(1)	89.41(11)
Complex <b>25</b>	
Ni(1)–N(1)	1.907(2)
Ni(1)–N(3)	1.917(2)
Ni(2)–N(4)	1.897(2)
Ni(2)–N(2)	1.912(3)
C(44)–C(45)	1.360(5)
C(45)–C(46)	1.491(6)
N(1)–Ni(1)–N(3)	94.06(10)
N(4)–Ni(2)–N(2)	94.37(10)
N(2)–Ni(1)–Ni(1)	118.68(19)

### 3. Summary

In summary, a new class of (CH<sub>2</sub>)<sub>n</sub>-bridged indenyl-pyrazoles were successfully synthesized and their reactions with nickelocene afforded trimetallic or dimetallic cyclopentadienyl nickel(II) pyrazolato complexes. These indenyl-pyrazoles are potentially useful precursors to dianionic ligands for constructing metal complexes.

### 4. Experimental

#### 4.1. General considerations

The synthetic reactions for preparation of the nickel(II) complexes were carried out under a nitrogen atmosphere with a dry-box and standard Schlenk techniques. Dried solvents were used in all experiments. Melting points are not corrected. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a 400 MHz NMR spectrometer and all chemical shift values refer to  $\delta_{\text{TMS}} = 0.00$  ppm or CDCl<sub>3</sub> ( $\delta(^1\text{H})$ , 7.26 ppm;  $\delta(^{13}\text{C})$ , 77.16 ppm). 2-Acetyl-3-hydroxy-2-butenolate (**1**), 2-benzoyl-3-hydroxy-2-butenolate (**2**), ethyl 3,5-dimethyl-1*H*-pyrazole-4-carboxylate (**3**), and 4-hydroxy-3,5-dimethyl-1*H*-pyrazole (**5**) [35], 1,1-diacetylcyclopropane (**9**), 1-acetyl-1-benzoyl-cyclopropane (**10**), and 4-(2-bromoethyl)-3,5-dimethyl-1*H*-pyrazole (**11**) [37,38] and ( $\beta$ -bromopropyl)indene (**15**) [39] were prepared as reported. All the other chemicals were analytical reagents and used as received.

#### 4.2. Synthesis of ethyl 3-methyl-5-phenyl-1*H*-pyrazole-4-carboxylate (**4**)

To a solution of ethyl 2-benzoyl-3-hydroxy-2-butenolate (**2**) (40.0 g, 0.17 mol) in 400 mL ethanol was added hydrazine dihydrochloride (20.0 g, 0.19 mol) in portions at ambient temperature over a period of 1 h. After the mixture was stirred for 24 h, all the volatiles were evaporated under reduced pressure, and the resultant residue was dissolved in 400 mL CH<sub>2</sub>Cl<sub>2</sub>. Cold aqueous KOH solution (1.80 M, 200 mL) was added and the organic layer was separated, and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 100 mL). The combined organic phase was dried over anhydrous MgSO<sub>4</sub>, filtered, and all the volatiles were removed under reduced pressure to yield **4** as a colorless oil (37.50 g, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 23 °C)  $\delta$  12.32 (br and s, 1H, N–H), 7.54 and 7.37 (m and br each, 2:3H, Ph), 4.18 (q, 2H, OCH<sub>2</sub>), 2.22 (s, 3H, Me of Pz), 1.19 (t, 3H, Me of Et); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)  $\delta$  164.14 (Cq, C=O), 152.24 and 147.67 (Cq each, C–N of Pz), 132.09 (Cq, *i*-C of Ph), 129.55, 128.73 and 127.93 (CH of Ph), 108.90 (Cq, C4 of Pz), 59.92 (OCH<sub>2</sub>), 14.14 and 12.10 (2 × Me). Anal. Calc. for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.76; H, 6.08; N, 12.31%.

#### 4.3. Synthesis of 4-hydroxy-3-methyl-5-phenyl-1*H*-pyrazole (**6**)

To a stirred suspension of LiAlH<sub>4</sub> (12.00 g, 0.32 mol) in 500 mL diethyl ether, a solution of compound **4** (37.00 g, 0.16 mol) in 200 mL diethyl ether and 20 mL THF was added dropwise at ambient temperature over a period of 4 h. The resulting mixture was stirred for 3 h and 50 mL water was then added dropwise to quench the reaction at 0 °C within 30 min. All the volatiles were removed under reduced pressure to result in a white cake which was suspended in 350 mL methanol, treated with carbon dioxide gas for 20 min, and then heated to reflux for 2 h. The precipitate was filtered, and extracted with boiling ethanol (5 × 200 mL). Evaporation of the solvent from the extract left a white solid which was successively washed with toluene (3 × 50 mL) and petroleum

ether (30–60 °C, 3 × 50 mL), affording **6** as white prisms (15.90 g, 55%). M.p.: 236 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz, 23 °C) δ 7.75, 7.41 and 7.30 (m each, 2:2:1 H, Ph), 4.35 (s, 2H, OCH<sub>2</sub>), 2.24 (s, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-*d*<sub>6</sub>, 23 °C) δ 147.31 and 142.47 (Cq, C–N of Pz), 133.48 (Cq, *i*-C of Ph), 129.03 and 128.01 (CH of Ph), 115.71 (C4 of Pz), 53.50 (CH<sub>2</sub>OH), 10.60 (CH<sub>3</sub>). Anal. Calc. for C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O: C, 70.19; H, 6.43; N, 14.88. Found: C, 69.98; H, 6.55; N, 14.82%.

#### 4.4. Synthesis of (Ind-CH<sub>2</sub>-PzH) (**7** and **8**)

A mixture of **5** or **6** and thionyl chloride (80 mL) was refluxed at 80 °C for 1 h. The unreacted thionyl chloride was removed by distillation, and the resultant residue was washed with petroleum ether (60–90 °C, 3 × 100 mL) and CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL) to afford chloride **5'** or **6'** as a white solid which was directly used for the next-step preparation. A mixture of indene and KH in THF was stirred at 0 °C to prepare indenylpotassium. After gas evolution ceased, a solution of **5'** or **6'** in THF was added dropwise to the freshly prepared indenylpotassium solution. The mixture was stirred at ambient temperature for 18 h and at 60 °C for 5 h, and then quenched with aqueous NH<sub>4</sub>Cl solution. Diethyl ether (200 mL) was added to perform a liquid–liquid extraction. The organic phase was collected, dried over anhydrous MgSO<sub>4</sub>, and concentrated under reduced pressure. The resultant viscous oil was purified by flash silica gel column chromatography with petroleum ether (60–90 °C)/ethyl acetate/Et<sub>3</sub>N, v/v 3:1:1) as the eluent to give the desired product.

**4-(1H-Inden-3-yl)methyl-3,5-dimethyl-1H-pyrazole (7)**. Treatment of **5'** (3.20 g, 25.4 mmol) with freshly prepared indenylpotassium (64.4 mmol) afforded **7** (1.54 g, 27%) as a pale yellow solid. M.p.: 125–126 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 23 °C) δ 10.20 (br and s, 1H, NH), 7.50, 7.44, 7.36 and 7.26 (m each, 1:1:1:1 H, aromatic CH), 5.96 (s, 1H, Ind-CH), 3.64 (d, Ind-CH<sub>2</sub>), 3.34 (s, 2H, CH<sub>2</sub>-Pz), 2.26 (s, 6H, 2 × Me); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 145.30, 144.82, 143.00, and 142.65 (Cq), 128.84, 126.16, 124.75, 123.88, and 118.94 (aromatic CH), 112.36 (Cq, C4 of Pz), 37.56 and 21.90 (2 × CH<sub>2</sub>), 11.04 (s, 2 × Me). Anal. Calc. for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.43; H, 7.15; N, 12.50%.

**4-(1H-Inden-3-yl)methyl-3-methyl-5-phenyl-1H-pyrazole (8)**. In a fashion similar to synthesis of **7**, the reaction of **6'** (2.85 g, 15.1 mmol) with indenylpotassium (81.8 mmol) afforded a pale brown oily residue which was recrystallized in acetone/hexane (v/v, 1:15) at –20 °C to give **8** (3.96 g, 68%) as pale yellow solid. M.p.: 102 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 23 °C) δ 7.55, 7.44, 7.35 and 7.28 (m each, 3:1:4:1 H, aromatic CH), 6.01 (t, 1H, Ind-CH), 3.78 (d, 2H, Ind-CH<sub>2</sub>), 3.37 (s, 2H, CH<sub>2</sub>Pz), 2.21 (s, 3H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 146.13, 145.14, 144.94, 144.32, and 143.07 (Cq), 131.73 (Cq, *i*-C of Ph), 129.37, 128.94, 128.24, 127.64, 126.28, 124.98, 123.99, and 119.00 (CH), 112.67 (Cq, C4 of Pz), 37.76 and 22.46 (2 × CH<sub>2</sub>), 10.92 (Me). Anal. Calc. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O.5acetone: C, 81.87; H, 6.71; N, 8.88. Found: C, 82.23; H, 6.73; N, 8.90%.

#### 4.5. Synthesis of 4-(2-bromoethyl)-3-methyl-5-phenyl-1H-pyrazole (**12**)

A mixture of **10** (10.30 g, 54.7 mmol), hydrazine (85%, 4.0 mL, 67.9 mmol) in 400 mL aqueous NH<sub>4</sub>Br solution (0.02 M) was stirred at ambient temperature for 24 h. The resulting mixture was extracted with CHCl<sub>3</sub> (2 × 100 mL), and the extract was dried over anhydrous MgSO<sub>4</sub>, concentrated under reduced pressure, and then recrystallized from hexane/ethyl acetate (v/v, 10:1) at –20 °C to give **12** as pale yellow crystals (8.52 g, 63%). M.p.: 91 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 23 °C) δ 10.20 (br and s, 1H, NH), 7.49 and 7.39 (m each, 2:3 H, Ph), 3.35 (t, 2H, CH<sub>2</sub>Br), 3.31 (t, 2H, CH<sub>2</sub>Pz), 2.17

(s, 3H, Me); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 146.93 and 143.08 (Cq, C–N of Pz), 132.18 (Cq, *i*-C of Ph), 129.00, 128.39 and 127.80 (2:1:2 CH, Ph), 113.01 (Cq, C4 of Pz), 31.88 and 27.65 (CH<sub>2</sub>), 10.74 (Me). Anal. Calc. for C<sub>12</sub>H<sub>13</sub>BrN<sub>2</sub>: C, 54.36; H, 4.94; N, 10.57. Found: C, 54.51; H, 4.95; N, 10.56%.

#### 4.6. Synthesis of (Ind-(CH<sub>2</sub>)<sub>2</sub>-PzH) (**13** and **14**)

To a stirred solution of indene in 100 mL THF was added *n*-BuLi (2.8 M in hexane) at –15 °C. The mixture was warmed up to ambient temperature to be stirred for 2 h and then cooled to 0 °C. Compound **11** or **12** in 10 mL THF was then added over a period of 30 min. The mixture was warmed up to ambient temperature and stirred for 12 h, then at 60 °C for 1.5 h. The reaction was quenched with 50 mL of saturated aqueous NH<sub>4</sub>Cl solution. Diethyl ether (100 mL) was added to perform a liquid–liquid extraction. The organic phase was separated and dried over anhydrous MgSO<sub>4</sub>. After all the volatiles were removed under reduced pressure, the resulting viscous oil was purified by flash silica gel column chromatography with petroleum ether (60–90 °C)/ethyl acetate/Et<sub>3</sub>N, v/v 4:4:1) as the eluent to give the product.

**4-(2-(1H-Inden-3-yl)ethyl)-3,5-dimethyl-1H-pyrazole (13)**. Reaction of **11** (7.00 g, 34.5 mmol) with indenyllithium (85.2 mmol) in THF afforded **13** as a colorless crystalline solid (6.45 g, 79%). M.p.: 114–115 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 23 °C) δ 10.15 (br and s, 1H, NH), 7.49, 7.36, 7.33, and 7.23 (m each, 1:1:1:1 H, aromatic CH), 6.23 (s, 1H, Ind-CH), 3.35 (s, 2H, Ind-CH<sub>2</sub>), 2.75 and 2.73 (m each, 2:2 H, 2 × CH<sub>2</sub>), 2.21 (s, 6H, 2 × Me); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) δ 145.40, 144.53, 144.17, and 142.16 (Cq), 128.41, 126.15, 124.67, 123.93, and 118.93 (CH), 115.31 (Cq, C4 of Pz), 37.89, 29.05 and 22.13 (3 × CH<sub>2</sub>), 10.97 (2 × Me). Anal. Calc. for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>: C, 80.63; H, 7.61; N, 11.75. Found: C, 80.85; H, 7.71; N, 11.74%.

**4-(2-(1H-Inden-3-yl)ethyl)-3-methyl-5-phenyl-1H-pyrazole (14)**. In a fashion similar to synthesis of **13**, reaction of **12** (3.00 g, 11.3 mmol) with indenyllithium (25.0 mmol) in THF afforded **14** as a pale brown oil (3.22 g, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 23 °C) δ 12.30 (br and s, 1H, NH), 7.59, 7.50, 7.41 and 7.30 (m each, 2:1:3:3 H, aromatic CH), 6.23 (s, 1H, Ind-CH), 3.34 (d, 2H, Ind-CH<sub>2</sub>), 2.97 and 2.75 (t each, 2:2 H, 2 × CH<sub>2</sub>), 2.13 (s, 3H, Me); <sup>13</sup>C{<sup>99</sup>H} NMR (CDCl<sub>3</sub>) δ 145.32, 144.46, and 144.06 (Cq), 133.10 (br and Cq, *i*-C of Ph), 128.65, 128.25, 127.91, 127.74, 126.07, 125.85, 124.61, 123.83, and 118.92 (CH), 115.29 (Cq, C4 of Pz), 37.83, 29.10, and 22.33 (3 × CH<sub>2</sub>), 10.51 (br, 2 × Me). Anal. Calc. for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.86; H, 6.87; N, 9.34%.

#### 4.7. Synthesis of (Ind-(CH<sub>2</sub>)<sub>3</sub>-PzH) (**16–19**)

The mixture of a β-diketone, (3-bromopropyl)indene (**15**), potassium carbonate, and potassium iodide in 50 mL acetone was refluxed for 48–72 h. After cooled to ambient temperature, the mixture was filtered. The filtrate was evaporated all the volatiles under reduced pressure and the resulting crude 3-(3-bromopropyl)indenyl-2,4-dione (**15'**) was further dried in vacuum at 100 °C for 5 h and followed by reacting with hydrazine in refluxing ethanol (50 mL) for 2 h. After cooled and concentrated in vacuo the resultant viscous oil was purified by flash silica gel column chromatography with petroleum ether (60–90 °C)/ethyl acetate/Et<sub>3</sub>N, v/v 4:4:1) as the eluent to give the product.

**4-(3-(1H-Inden-3-yl)propyl)-3,5-dimethyl-1H-pyrazole (16)**. Alkylation of acetoacetone (2.00 g, 56.7 mmol) with **15** (4.23 g, 17.8 mmol) in the presence of K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20.0 mmol) and KI (1.48 g, 8.9 mmol) produced **15'** as a colorless oil which was directly reacted with hydrazine hydrate (85%, 3.0 mL, 50.9 mmol) in refluxing ethanol (50 mL) to afford **16** as a white solid (2.33 g, 52%). Colorless crystals were obtained by recrystallization in hex-

ane at  $-20^{\circ}\text{C}$ . M.p.:  $101\text{--}102^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.46, 7.29 and 7.20 (m each, 1:2:1 H, aromatic CH), 6.21 (s, 1H, Ind-CH), 3.34 (br, 2H, Ind- $\text{CH}_2$ ), 2.56 and 2.48 (t each, 2:2 H,  $2 \times \text{CH}_2$ ), 2.23 (s, 6H,  $2 \times \text{Me}$ ), 1.87 (m, 2H,  $\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.56, 144.59, 144.36, and 142.22 (Cq), 127.73, 126.09, 124.63, 123.8 and 118.95 (CH), 115.00 (Cq, C4 of Pz), 37.83, 28.84, 27.38, and 23.06 ( $4 \times \text{CH}_2$ ), 11.04 ( $2 \times \text{Me}$ ). Anal. Calc. for  $\text{C}_{17}\text{H}_{20}\text{N}_2$ : C, 80.91; H, 7.99; N, 11.10. Found: C, 81.22; H, 7.87; N, 11.01%.

**4-(3-(1H-Inden-3-yl)propyl)-3,5-di-tert-butyl-1H-pyrazole (17)**. In a fashion similar to synthesis of **16**, a mixture of 2,2,6,6-tetramethyl-3,5-heptanedione (0.82 g, 4.4 mmol), **15** (1.00 g, 4.2 mmol), potassium carbonate (0.61 g, 4.4 mmol), and potassium iodide (0.37 g, 2.2 mmol) in 50 mL acetone was refluxed for 48 h to give 3-(3-indenylpropyl)-2,4-dione which was then reacted with hydrazine hydrate (85%, 0.25 mL, 4.2 mmol) in the presence of three drops of concentrated hydrochloric acid in 15 mL refluxing ethanol for 18 h. The work-up procedure resulted in an oily material which was recrystallized in acetone at  $-20^{\circ}\text{C}$ , affording **17** as colorless crystals (0.62 g, 55%). M.p.:  $184\text{--}185^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.50, 7.41, 7.33, and 7.25 (m each, 1:1:1:1 H, aromatic CH), 6.27 (s, 1H, Ind-CH), 3.37 (br, 2H, Ind- $\text{CH}_2$ ), 2.75, 2.69, and 2.00 (m each, 2:2:2 H,  $3 \times \text{CH}_2$ ), 1.38 (s, 18H,  $6 \times \text{Me}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  153.69, 145.52, 144.58, 144.22, and 113.67 (Cq), 128.18, 126.09, 124.63, 123.87, 119.01 (CH), 37.82, 32.84 (Cq), 31.17, 30.39 ( $6 \times \text{Me}$ ), 28.42, 25.34. Anal. Calc. for  $\text{C}_{23}\text{H}_{32}\text{N}_2$ : C, 82.09; H, 9.58; N, 8.32. Found: C, 82.07; H, 9.60; N, 8.34%.

**4-(3-(1H-Inden-3-yl)propyl)-3-methyl-5-phenyl-1H-pyrazole (18)**. Alkylation of acetylbenzoylmethane (2.36 g, 14.6 mmol) with **15** (3.45 g, 14.6 mmol) in the presence of  $\text{K}_2\text{CO}_3$  (2.42 g, 17.5 mmol) and KI (1.21 g, 7.3 mmol) produced **15'** which was directly reacted with hydrazine hydrate (85%, 5.0 mL, 85.0 mmol) in refluxing ethanol (50 mL) to afford **18** as a light brown oil (2.40 g, 52%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  8.70 (br and s, 1H, NH), 7.49, 7.32, 7.30, and 7.23 (m each, 3:3:2:1 H, aromatic CH), 6.14 (s, 1H, Ind-CH), 3.30 (d, 2H, Ind- $\text{CH}_2$ ), 2.66 and 2.54 (m each, 2:2 H,  $2 \times \text{CH}_2$ ), 2.24 (s, 3H, Me), 1.90 (m, 2H,  $\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  145.99, 145.46, 144.60, 144.04, and 142.95 (Cq), 132.74 (Cq, *i*-Cq of Ph), 128.67, 128.10, 127.80, 126.09, 124.59, 123.82, and 119.02 (CH), 115.64 (Cq, C4 of Pz), 37.80, 28.85, and 23.27 ( $3 \times \text{CH}_2$ ), 10.88 (Me). Anal. Calc. for  $\text{C}_{22}\text{H}_{22}\text{N}_2$ : C, 84.04; H, 7.05; N, 8.91. Found: C, 84.08; H, 7.06; N, 8.84%.

**4-(3-(1H-Inden-3-yl)propyl)-3,5-diphenyl-1H-pyrazole (19)**. Alkylation of dibenzoylmethane (3.80 g, 16.9 mmol) with **15** (4.00 g, 16.9 mmol) in the presence of  $\text{K}_2\text{CO}_3$  (2.34 g, 16.9 mmol) and KI (1.40 g, 8.4 mmol) produced **15'** which was directly reacted with hydrazine hydrate (85%, 3.0 mL, 50.9 mmol) in the presence of three drops of 37% hydrochloric acid in refluxing ethanol (50 mL) to afford **19** as a pale yellow solid (3.46 g, 54%). Colorless crystals were obtained by recrystallization from acetone and hexane (v/v, 1:3) at  $-20^{\circ}\text{C}$ . M.p.:  $154^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.54, 7.44, 7.36, 7.22 and 7.13 (m each, 4:1:6:2:1 H, aromatic CH), 5.99 (s, 1H, Ind-CH), 3.23 (d, 2H, Ind- $\text{CH}_2$ ), 2.85 and 2.46 (t each, 2:2 H,  $2 \times \text{CH}_2$ ), 1.84 (m, 2H,  $\text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  146.73 (Cq and br), 145.38, 144.58, and 143.74 (Cq), 132.30 (Cq, *i*-Cq of Ph), 128.78, 128.32, 128.12, 127.98, 126.06, 124.52, 123.77, and 119.06 (CH), 115.86 (Cq, C4 of Pz), 37.74, 28.72, 27.61, and 23.34 ( $4 \times \text{CH}_2$ ). Anal. Calc. for  $\text{C}_{27}\text{H}_{24}\text{N}_2$ : C, 86.13; H, 6.43; N, 7.44. Found: C, 86.02; H, 6.48; N, 7.38%.

#### 4.8. Synthesis of complexes $[\text{CpNi}\{\text{Ind}-(\text{CH}_2)_n\text{-Pz}\}_2]_2\text{Ni}$ (**20–24**) and $[\text{CpNi}\{\text{Ind}-(\text{CH}_2)_3\text{-Pz}\}_2]$ (**25**) – a general procedure

A mixture of nickelocene ( $\text{Cp}_2\text{Ni}$ ) and an indenyl-pyrazole in 1:1 molar ratio was stirred in refluxing toluene, forming a deep-red solution. All the volatiles were removed under reduced pressure and the resultant residue was extracted with toluene, filtered

through a short pad of celite. The filtrate was concentrated under reduced pressure and the resulting crude product was purified by flash silica gel column chromatography with toluene as the eluent, affording complexes **20–25** as the products.

$[\text{CpNi}\{4-(1\text{H-inden-3-yl)methyl-3,5-dimethylpyrazolato}\}_2]_2\text{Ni}$  (**20**). A mixture of nickelocene (126 mg, 0.67 mmol), **7** (150 mg, 0.67 mmol) and 10 mL toluene was refluxed for 3 h afforded complex **20** as red crystalline solid (103 mg, 52%). M.p.:  $>182^{\circ}\text{C}$ , dec.  $^1\text{H}$  NMR (toluene- $d_8$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.27 and 7.10 (m each, 12:4 H, aromatic CH), 5.50 (s, 10H,  $2 \times \text{Cp}$ ), 4.54 (s, 4H,  $2 \times \text{Ind-CH}$ ), 3.30 and 2.85 (m each, 8:8 H,  $8 \times \text{CH}_2$ ), 2.29 and 2.10 (s each, 24H,  $8 \times \text{Me}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ )  $\delta$  151.79, 151.40, 146.42, 145.67, and 145.03 (Cq), 129.00, 126.98, 124.61, and 119.76 (aromatic CH), 115.63 (Cq, C4 of Pz), 93.97 (Cp), 38.14 and 23.80 ( $\text{CH}_2$ ), 15.50 and 13.33 (Me). Anal. Calc. for  $\text{C}_{70}\text{H}_{70}\text{N}_8\text{Ni}_3$ : C, 70.10; H, 5.88; N, 9.34. Found: C, 70.20; H, 5.89; N, 9.37%.

$[\text{CpNi}\{4-(1\text{H-inden-3-yl)methyl-3-methyl-5-phenylpyrazolato}\}_2]_2\text{Ni}$  (**21**). In a fashion similar to synthesis of **20**, a mixture of nickelocene (132 mg, 0.70 mmol), **8** (200 mg, 0.70 mmol) and 10 mL toluene was refluxed for 2 h afforded complex **21** as red crystalline solid (163 mg, 48%). M.p.:  $>162^{\circ}\text{C}$ , dec.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.44 and 7.21 (m each, 24:12 H, aromatic CH), 5.69 (br, 4H, Ind-CH), 4.30 (s, 10H,  $2 \times \text{Cp}$ ), 3.38 and 3.19 (m each, 8:8 H,  $8 \times \text{CH}_2$ ), 2.28 (s, 12H,  $4 \times \text{Me}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  157.77, 151.57, 145.37, 144.69, and 144.30 (Cq), 136.17 (Cq, *i*-Cq of Ph), 130.65, 128.65, 127.92, 126.07, 124.63, 123.75, and 118.97 (CH), 115.73 (Cq, C4 of Pz), 93.75 (Cp), 37.5 and 23.01 ( $2 \times \text{CH}_2$ ), 12.47 (Me). Anal. Calc. for  $\text{C}_{90}\text{H}_{78}\text{N}_8\text{Ni}_3$ : C, 74.67; H, 5.43; N, 7.74. Found: C, 74.51; H, 5.40; N, 7.69%.

$[\text{CpNi}\{4-(2-(1\text{H-inden-3-yl)ethyl)-3,5-dimethylpyrazolato}\}_2]_2\text{Ni}$  (**22**). In a fashion similar to synthesis of **20**, a mixture of nickelocene (159 mg, 0.84 mmol), **13** (200 mg, 0.84 mmol) and 10 mL toluene was refluxed for 3 h afforded complex **22** as a red solid (220 mg, 84%). Single crystals suitable for X-ray crystallographic determination were grown from recrystallization in toluene at  $-20^{\circ}\text{C}$ . M.p.:  $198^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.44, 7.25 and 7.17 (m each, 4:4:8 H, aromatic CH), 6.09 (s, 4H, Ind-CH), 5.64 (s, 10H,  $2 \times \text{Cp}$ ), 3.27 (br, 8H,  $4 \times \text{Ind-CH}_2$ ), 2.49 and 2.37 (m each, 8:8 H,  $8 \times \text{CH}_2$ ), 2.15 (s,  $8 \times \text{Me}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  150.41, 150.27, 145.43, 144.51, and 144.43 (Cq), 127.86, 126.03, 124.49, 123.77, and 118.93 (CH), 117.92 (Cq, C4 of Pz), 93.12 (Cp), 37.78, 29.84, and 23.44 ( $3 \times \text{CH}_2$ ), 14.68 and 12.15 ( $2 \times \text{Me}$ ). Anal. Calc. for  $\text{C}_{74}\text{H}_{78}\text{N}_8\text{Ni}_3 \cdot 2\text{PhMe}$ : C, 73.41; H, 6.58; N, 7.78. Found: C, 73.01; H, 6.56; N, 7.75%.

$[\text{CpNi}\{4-(3-(1\text{H-inden-3-yl)propyl)-3,5-dimethylpyrazolato}\}_2]_2\text{Ni}$  (**23**). In a fashion similar to synthesis of **20**, a mixture of nickelocene (150 mg, 0.79 mmol), **16** (200 mg, 0.79 mmol) and 10 mL toluene was refluxed for 5 h to afford complex **23** as a red solid (203 mg, 78%). Single crystals suitable for X-ray crystallographic determination were grown from recrystallization in hexane/ $\text{CH}_2\text{Cl}_2$  (v/v, 5/1) at  $-20^{\circ}\text{C}$ . M.p.:  $172^{\circ}\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.39, 7.27 and 7.15 (m each, 1:1:2 H, aromatic CH), 5.96 (s, 4H,  $4 \times \text{Ind-CH}$ ), 5.63 (s, 10H,  $2 \times \text{Cp}$ ), 3.14 (br, 8H,  $4 \times \text{Ind-CH}_2$ ), 2.21, 2.14, and 1.47 (br each, 24H,  $12 \times \text{CH}_2$ ), 2.07 (s, 24H,  $8 \times \text{Me}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  150.30, 145.60, 144.56, and 144.42 (Cq), 127.47, 125.90, 124.43, 123.74, and 118.8 (CH), 118.08 (Cq, C4 of Pz), 93.09 (Cp), 37.64, 29.54, 27.09 and 24.27 ( $\text{CH}_2$ ), 14.82 and 12.16 (Me). Anal. Calc. for  $\text{C}_{78}\text{H}_{86}\text{N}_8\text{Ni}_3$ : C, 71.42; H, 6.61; N, 8.54. Found: C, 71.72; H, 6.65; N, 8.49%.

$[\text{CpNi}\{4-(3-(1\text{H-inden-3-yl)propyl)-3methyl-5-phenylpyrazolato}\}_2]_2\text{Ni}$  (**24**). In a fashion similar to synthesis of **20**, a mixture of nickelocene (135 mg, 0.71 mmol), **18** (224 mg, 0.71 mmol) and 10 mL toluene was refluxed for 2 h to afford complex **24** as a red solid (105 mg, 38%). M.p.:  $>142^{\circ}\text{C}$ , dec.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz,  $23^{\circ}\text{C}$ )  $\delta$  7.50 and 7.17 (m each, 24:12 H, aromatic CH), 5.95 (s, 4H,  $4 \times \text{Ind-CH}$ ), 4.24 (s, 10H,  $2 \times \text{Cp}$ ), 3.17 (br, 8H, Ind- $\text{CH}_2$ ),

2.28, 2.13, and 1.53 (br each, 8:8:8 H,  $12 \times \text{CH}_2$ ), 2.12 (s, 12H,  $4 \times \text{Me}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  157.06, 150.96, 145.59, 144.58, and 144.22 (Cq), 136.71 (Cq, *i*-C of Ph), 130.85, 128.37, 127.90, 127.74, 127.60, 125.97, 124.46, 123.76, and 118.91 (CH), 119.34 (Cq, C4 of Pz), 93.55 (Cp), 37.70, 29.83, 27.52, and 24.19 ( $\text{CH}_2$ ), 11.96 (Me). Anal. Calc. for  $\text{C}_{98}\text{H}_{94}\text{N}_8\text{Ni}_3$ : C, 73.93; H, 5.92; N, 7.84. Found: C, 73.87; H, 5.85; N, 7.73%.

$[\text{CpNi}\{4-(3-(1\text{H-inden-3-yl)propyl})-3,5\text{-diphenylpyrazolato}\}]_2$  (**25**).

In a fashion similar to synthesis of **20**, a mixture of nickelocene (52 mg, 0.28 mmol), **19** (102 mg, 0.28 mmol) and 5 mL toluene was refluxed for 1 h to afford complex **25** as a red-purple crystalline solid (72 mg, 82%). Single crystals suitable for X-ray crystallographic determination were grown from dichloromethane/hexane (v/v, 1/5) at  $-20^\circ\text{C}$ . M.p.:  $>154^\circ\text{C}$ , dec.  $^1\text{H}$  NMR (toluene- $d_8$ , 400 MHz,  $23^\circ\text{C}$ )  $\delta$  7.93, 7.41, 7.28 and 6.92 (m each, 8:8:6:6 H, aromatic CH and Ph), 5.59 (s, 2H,  $2 \times \text{Ind-CH}$ ), 3.87 (s, 10H,  $2 \times \text{Cp}$ ), 2.88 (br, 4H,  $2 \times \text{Ind-CH}_2$ ), 2.63, 2.11, and 1.62 (br each, 4:4:4 H,  $6 \times \text{CH}_2$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )  $\delta$  162.71, 146.57, 145.36, and 145.00 (Cq), 137.52 (Cq, *i*-C of Ph), 131.47, 128.88, 128.40, 128.09, 126.86, 125.24, 124.44, and 119.97 (CH), 122.07 (Cq, C4 of Pz), 96.56 (Cp), 38.31, 30.86, 28.43, and 25.97 ( $\text{CH}_2$ ). Anal. Calc. for  $\text{C}_{64}\text{H}_{56}\text{N}_4\text{Ni}_2$ : C, 74.69; H, 5.34; N, 6.45. Found: C, 74.87; H, 5.26; N, 6.48%.

#### 4.9. X-ray crystallographic studies

Single crystal X-ray crystallographic studies for compounds **16**, **22**, **23**, and **25** were carried out on a X-ray diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$ . All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. Crystal data and refinement details for these compounds are summarized in Table 1.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.10.021.

#### References

- [1] A.P. Sadimenko, Adv. Heterocycl. Chem. 39 (2001) 157.
- [2] J.E. Cosgriff, G.B. Deacon, Angew. Chem., Int. Ed. 37 (1998) 286.
- [3] G. La Monica, G.A. Arduozzo, Prog. Inorg. Chem. 46 (1997) 151.
- [4] A.P. Sadimenko, S.S. Basson, Coord. Chem. Rev. 147 (1996) 247.
- [5] S. Trofimenko, Polyhedron 23 (2004) 197.
- [6] S. Trofimenko, Chem. Rev. 93 (1993) 943.
- [7] J.R. Perera, M.J. Heeg, H.B. Schlegel, C.H. Winter, J. Am. Chem. Soc. 121 (1999) 4536.
- [8] J.R. Perera, M.J. Heeg, C.H. Winter, Organometallics 19 (2000) 5263.
- [9] G.B. Deacon, C.M. Forsyth, A. Gitlits, R. Harika, P.C. Junk, B.W. Skelton, A.H. White, Angew. Chem., Int. Ed. 41 (2002) 3249.
- [10] P. Espinet, K. Soulantica, Coord. Chem. Rev. 193–195 (1999) 499.
- [11] J.-C. Hierso, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier, P. Kalck, Coord. Chem. Rev. 236 (2003) 143.
- [12] F.L. Zeng, Z.K. Yu, Organometallics 27 (2008) 2898.
- [13] C.L. Dezelah IV, M.K. Wiedmann, K. Mizohata, R.J. Baird, L. Niinistö, C.H. Winter, J. Am. Chem. Soc. 129 (2007) 12370.
- [14] C.T. Qian, W.L. Nie, J. Sun, J. Organomet. Chem. 626 (2001) 171.
- [15] W.L. Nie, C.T. Qian, Y.F. Chen, J. Sun, J. Organomet. Chem. 647 (2002) 114.
- [16] C.F. Pi, Z.X. Zhang, R.T. Liu, L.H. Weng, Z.X. Chen, X.G. Zhou, Organometallics 25 (2006) 5165.
- [17] J.R. Ascenso, A.R. Dias, J.A. Fernandes, A.M. Martins, S.S. Rodrigues, Inorg. Chim. Acta 356 (2003) 279.
- [18] S.W. Wang, X.L. Tang, A. Vega, J.-Y. Saillard, E.H. Sheng, G.S. Yang, S.L. Zhou, Z.X. Huang, Organometallics 25 (2006) 2399.
- [19] S.W. Wang, S.L. Zhou, E.H. Sheng, M.H. Xie, K.H. Zhang, L. Cheng, Y. Feng, L.L. Mao, Z.X. Huang, Organometallics 22 (2003) 3546.
- [20] E.H. Sheng, S.W. Wang, G.S. Yang, S.L. Zhou, K.H. Zhang, L. Cheng, Z.X. Huang, Organometallics 22 (2003) 684.
- [21] S.P. Downing, S.C. Guadaño, D. Pugh, A.A. Danopoulos, R.M. Bellabarba, M. Hanton, D. Smith, R.P. Tooze, Organometallics 26 (2007) 3762.
- [22] H.-M. Sun, D.-M. Hu, Y.-S. Wang, Q. Shen, Y. Zhang, J. Organomet. Chem. 692 (2007) 903.
- [23] J.C. Röder, F. Meyer, M. Konrad, S. Sandhöfner, E. Kaifer, H. Pritakow, Eur. J. Org. Chem. (2001) 4479.
- [24] A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejada, A. Lara-Sánchez, L. Sánchez-Barba, A.M. Rodríguez, M.A. Maestro, J. Am. Chem. Soc. 126 (2004) 1330.
- [25] A. Otero, J. Fernández-Baeza, A. Antiñolo, J. Tejada, A. Lara-Sánchez, L. Sánchez-Barba, M. Sanchez-Molina, A.M. Rodríguez, C. Bo, M. Urbano-Cuadrado, Organometallics 26 (2007) 4310.
- [26] A. Otero, J. Fernández-Baeza, A. Antiñolo, A. Lara-Sánchez, E. Martínez-Caballero, J. Tejada, L.F. Sánchez-Barba, C. Alonso-Moreno, I. López-Solera, Organometallics 27 (2008) 976.
- [27] J.C. Röder, F. Meyer, H. Pritzkow, Organometallics 20 (2001) 811.
- [28] S.J. Rettig, A. Storr, D.A. Summers, R.C. Thompson, J. Trotter, Can. J. Chem. 75 (1997) 949.
- [29] A. Storr, D.A. Summers, R.C. Thompson, Can. J. Chem. 76 (1998) 1130.
- [30] A.B. Blake, D. Ewing, J.E. Hamin, J.M. Lockyer, J. Chem. Soc., Dalton Trans. 19 (1977) 1897.
- [31] X.J. Sun, Z.K. Yu, S.Z. Wu, W.-J. Xiao, Organometallics 24 (2005) 2959.
- [32] H.X. Deng, Z.K. Yu, J.H. Dong, S.Z. Wu, Organometallics 24 (2005) 4110.
- [33] F.L. Zeng, Z.K. Yu, J. Org. Chem. 71 (2006) 5274.
- [34] W.Q. Tan, X.D. Zhao, Z.K. Yu, J. Organomet. Chem. 692 (2007) 5395.
- [35] J.-C. Jung, E.B. Watkins, M.A. Avery, Tetrahedron 58 (2002) 3639.
- [36] G.E. Mertzanos, J. Stephanidou-Stephanatou, C.A. Tsoleridis, Synth. Commun. 27 (1997) 493.
- [37] N.S. Zefirov, T.S. Kuznetsova, S.I. Kozhushkov, L.S. Surmina, Z.A. Rashchupkina, J. Org. Chem. USSR (Engl. Transl.) 19 (1983) 474.
- [38] N.S. Zefirov, S.I. Kozhushkov, T.S. Kuznetsova, Tetrahedron 38 (1982) 1693.
- [39] M. Makosza, Tetrahedron Lett. 38 (1966) 4621.