Pyrazole-Tethered Heteroditopic Ligands and Their Transition Metal Complexes: Synthesis, Structure, and Reactivity

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Various pyrazole-based P,N (**2a–c**) and N,N (**3a–b**) ligands have been synthesized. Using representative ligands, Ni^{II}, Co^{II}, Cu^{II}, and Cu^{I} complexes have been prepared and structurally characterized by crystallography. During complexation of Co^{II} and Cu^{II} salts, the phosphane part of the P,N ligand oxidized to phosphane oxide. For N,N donor ligands, a dimeric chloro-bridged Ni^{II} complex was obtained. Ni^{II} complex **4** is an active catalyst for ethylene oligomerization.

Introduction

Trofimenko[1] introduced pyrazole as a unique donor in coordination chemistry as tris(pyrazolyl)borate (Tp) and related ligands during late 1960s and early 1970s. A rich and parallel chemistry of Tp and its analogs[2] (often called 'scorpionates') developed subsequently in relation to metal-cyclopentadienyl complexes. Bidentate bis-pyrazolyl ligands are also known[3] and mixed donor ligands (pyrazole in combination with another type of donor atom or group) are currently gaining prominence, especially for their ability to stabilize different metals in diverse oxidation states.

The use of hemilabile ligands in coordination and organometallic chemistry has increased recently because of their potential application in catalysis. They are multidentate ligands that feature one weakly coordinating donor. This donor atom readily dissociates from the metal during catalysis, to accommodate reacting groups on the metal, but recombines with the metal when a coordinative unsaturation develops to stabilize the catalytic intermediate. Mixed ligands containing phosphorus along with oxygen, nitrogen or sulfur donor atoms have been designed in catalytic reactions such as ethylene polymerization,[4] the Heck reaction,[5] Suzuki coupling.[6] Hybrid P,N-type ligands confer high reactivity and selectivity in several catalytic reactions.[7] In continuation of our interest in developing pyrazole-based chelates,[8] we initiated a program for the design and synthesis of mixed donor ligands featuring substituted pyrazoles.

We intended to examine a set of new ligands for late transition elements, especially those relevant for catalysis of C–C (polymerization, Suzuki, Heck, Sonogashira) and C–N (aromatic amination) bond formation. We recently reported preliminary results of Suzuki and amination reactions featuring pyrazole-tethered phosphanes.[9a] Here, we report in detail the synthesis and complete characterization of those ligands and their late transition metal complexes, and initial observations on the application of a typical nickel complex in ethylene oligomerization.

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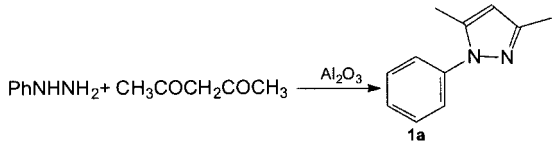
Results and Discussions

Synthesis of Ligands

Of the two sets of bidentate ligands used in the present study, one has a phosphane (**2a–c)** and other an amine (**3a–b**) in combination with pyrazole moiety.

3,5-Dimethyl-*N*-phenylpyrazole was synthesized by the action of acetylacetone with phenylhydrazine[10] (Scheme 1). This method was suitable when 3 and 5 substituents of pyrazole were identical. To synthesize unsymmetrically substituted pyrazoles (**1b** and **1c**) we followed an alternative route whereby substituted pyrazoles are coupled with phenylboronic acid by copper acetate in the presence of pyridine[11] (Scheme 2). This procedure provided regiochemically pure derivatives – the bulky substituent (*t*Bu or mesityl) is confined to 3-position of the pyrazole. Compounds **1a–c**, were characterized unambiguously by their ^{1}H and ^{13}C NMR spectroscopic data.



Scheme 1.

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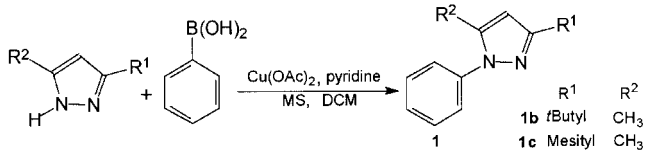
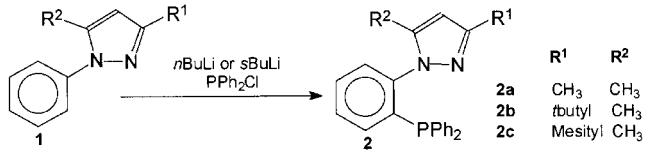


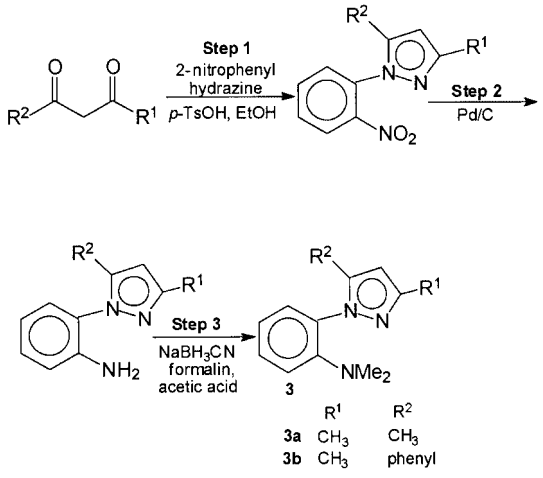
Scheme 2.

Directed lithiation on **1a** and **1b** at 0 °C using *n*BuLi and quenched with PPh_2Cl afforded the potentially bidentate ligands **2a** and **2b** (Scheme 3). Lithiation of **1c** proved difficult and required *s*BuLi. Compounds **2a**–**c** are solids that were purified by column chromatography or crystallization and characterized by spectroscopic data and elemental analysis.[9b] ^{31}P NMR absorptions appear at –23.89 (**2a**), –13.23 (**2b**) and –20.70 (**2c**) ppm.



Scheme 3.

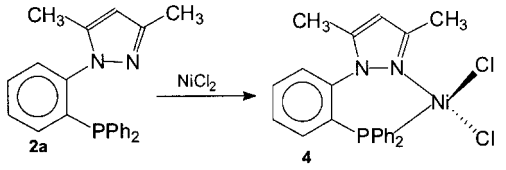
To prepare a set of ligands with nitrogen as a donor in place of phosphane we treated 2-nitrophenylhydrazine with acetylacetone or benzoylacetone followed by reduction of the nitro group with Pd/C. Reductive methylation of the resulting amine afforded the desired ligand (**3**) (Scheme 4). Reaction of benzoylacetone yielded only one product regioisomer, indicating that the hydrazine preferentially attacks the acetyl group.



Scheme 4.

Preparation of Metal Complexes

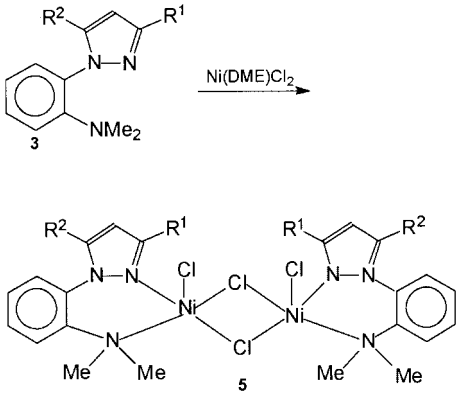
Ligand **2a** was used to synthesize representative transition metal complexes. Addition of a solution of ligand **2a** in acetonitrile to anhydrous $NiCl_2$ dissolved in acetonitrile resulted in a change of colour from yellow to violet after refluxing for 6 h, affording a violet precipitate as product. Complex **4** was isolated by filtration and recrystallized from acetonitrile to provide an analytically pure sample (Scheme 5). The NMR spectrum of this high-spin complex could not be recorded.



Scheme 5.

A single crystal of complex **4** suitable for structure analysis was grown in acetonitrile solution. Figure 1 depicts an ORTEP view of the so-determined molecular structure of **4**. A distorted tetrahedral geometry is seen around the nickel in a six-membered ring. It is strongly similar to a phosphanylaryl oxazoline complex[12] in terms of geometrical parameters, except that the difference in bond lengths of two Ni–halide bonds [0.021 Å between Ni–Cl1, 2.180(2) Å, and Ni–Cl, 2 2.201(2) Å] in **4** is more pronounced than in the reported complex (0.008 Å).

Nickel(II) complexes **5a** and **5b** were synthesized by the addition of ligands **3a** and **3b** to a solution of [Ni(DME)-Cl_2] in dichloromethane, resulting in an instant colour change from yellow to bright orange. A reddish orange solid was then filtered off and purified by crystallization from acetonitrile (Scheme 6). The crystal structure of **5b** (Figure 2) was then determined, revealing a bridged dinuclear species. The N3–Ni–Cl2A [170.4(4)°] bond angle is close to 180° while N1–Ni–N3 [83.18(5)°], Ni–Cl2–Ni1A [91.44(2)°] and N3–Ni–Cl1 [94.74(4)°] are close to 90°, establishing a square-pyramidal structure of complex **5b**. The Ni–Ni1A bond is 3.44 Å long.



Scheme 6.

Addition of a solution of ligand **2a** in acetonitrile to anhydrous $CoCl_2$ dissolved in acetonitrile resulted in an instant color change, from pale blue to deep blue. The reaction mixture was then stirred and heated under reflux for 6 h. Complex **6** was collected by filtration and crystallized from hot acetonitrile to afford blue needle-shaped crystals. The NMR spectra could not recorded, as the product was paramagnetic. Ligand **2a** reacts with anhydrous $CuCl_2$ in

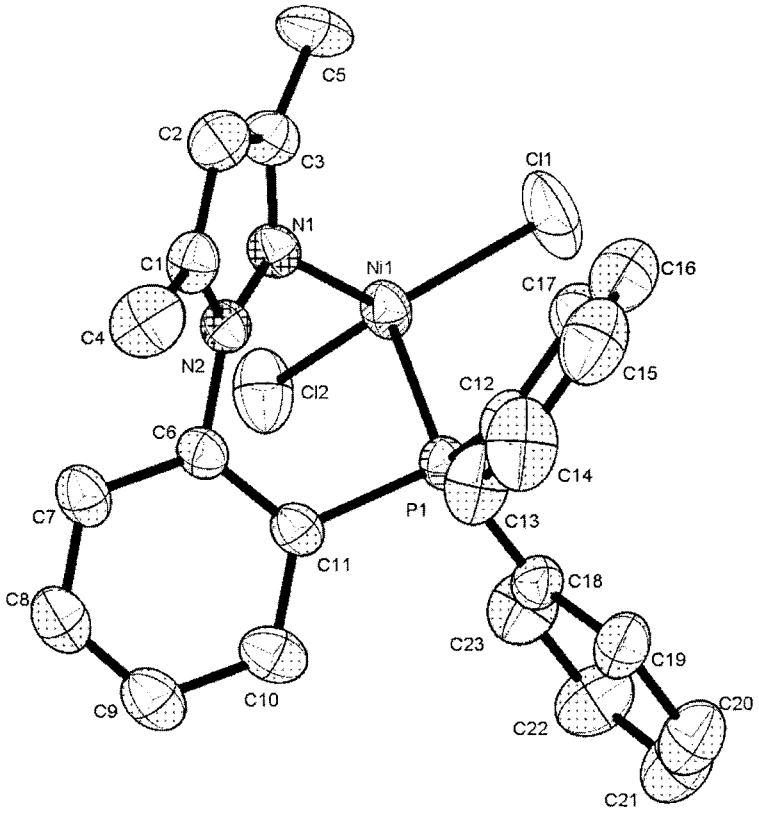
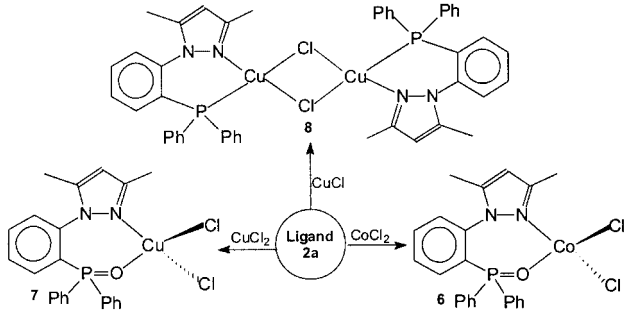


Figure 1. ORTEP diagram of Ni^{II} complex 4; ellipsoids drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: N1–N2 1.373(5), Ni–N1 2.003(4), Ni–Cl1 2.180(2), Ni–Cl2 2.201(2), Ni–P1 2.281(2). N1–Ni–P1 88.22(12), Cl1–Ni–Cl2 121.29(8), N2–N1–Ni 123.0(3), N1–Ni–Cl1 123.82 (14), N1–Ni–Cl2 104.07(13).

acetonitrile under identical conditions to furnish bright green, paramagnetic crystals of complex **7** (Scheme 7). Conversely, the reaction of ligand **2a** with CuCl in acetonitrile took 12 h to ensure a substantial reaction. Product **8** was obtained as a pale yellow powder, which was recrystallized from acetonitrile to obtain X-ray grade crystals.



Scheme 7.

Crystal structures of complexes **6**–**8** were determined. Interestingly, the Co^{II} and Cu^{II} complexes **6** and **7** are both seven-membered chelates, where the phosphane has been converted into phosphane oxide and the ligand **2a** is coordinated to the metal through the oxygen rather than phosphorus (Figure 3 and Figure 4). For complex **7**, the angle Cu–O–P [122.40(11)°] is suggestive of an sp^2-hybridized oxygen, unlike in $Cu(TPPO)_2Cl_2$ where the angle is considerably greater [Cu–O–P 150.9(3)°].[13a] The Co–O–P bond angle in **6** is 121.72(6)°, which is comparable with that in **7**, but smaller than the Co–O–P angle (153°) in $CoCl_2(OPPh_3)_2$.[13b] Co–O [1.991(11) Å] and P–O [1.507(12) Å] bond lengths in **6** are also comparable with those in **7** {Cu–O [1.995(18) Å] and P–O [1.506(18) Å]}. The P–O bonds of **6** [1.507(12) Å] and 7 [1.506(18) Å] are longer than that of free Ph_3PO [1.46(1) Å].

The Cu^I complex **8**, however, revealed a chloro-bridged, dimeric structure (Figure 5) that has an inversion symmetry overall, and a molecule of the solvent acetonitrile. The copper centers of **8** are 3.101 Å apart, which is comparable with the Cu–Cu′ bond length [3.066(1) Å] of the complex $[(PCy_3)CuCl]_2$.[13c] The Cu–P bond length [2.220(9) Å] of **8** is longer than Cu–P [2.183(2) Å] that of $[(PCy_3)CuCl]_2$. The ^1H NMR spectrum of this diamagnetic complex **8** displays sharp signals – three-proton methyl signals appear at different positions compared to the parent ligand (2.40 and 1.81 ppm in **8** vis-a-vis 2.19 and 2.00 ppm in ligand **2a**). One of the methyl signals in the complex is broad, indicating stereochemical non-rigidity in the molecule. The relative shielding of the methyl signal (δ = 1.81 ppm vs. 2.00 ppm) is possibly a reflection of the anisotropic effect – one methyl group lies in the shielding zone of a neighboring phenyl ring The pyrazole-4H appears at δ = 5.69 ppm, shifted upfield

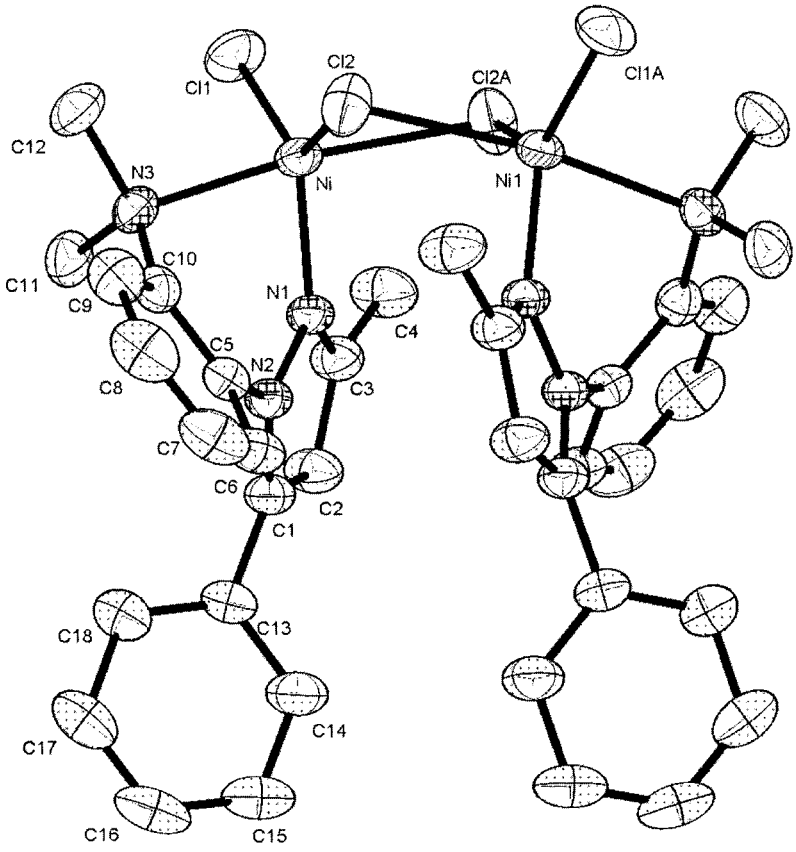


Figure 2. ORTEP diagram of Ni complex **5b**; ellipsoids drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Ni–N1 2.025(2), Ni–N3 2.210(2), Ni–Cl1 2.281(7), Ni–Cl2 2.349(9), Ni–Cl2A 2.461(9), Cl2–Ni2A 2.461(9). N1–Ni–N3 83.18(5), Ni–Cl2–Ni1A 91.44(2), N3–Ni–Cl1 94.74(4), N1–Ni–Cl2 121.61(4), N1–Ni–Cl1 108.03(5), Cl1–Ni–Cl2 130.36(3), N3–Ni–Cl2A 170.4(4).

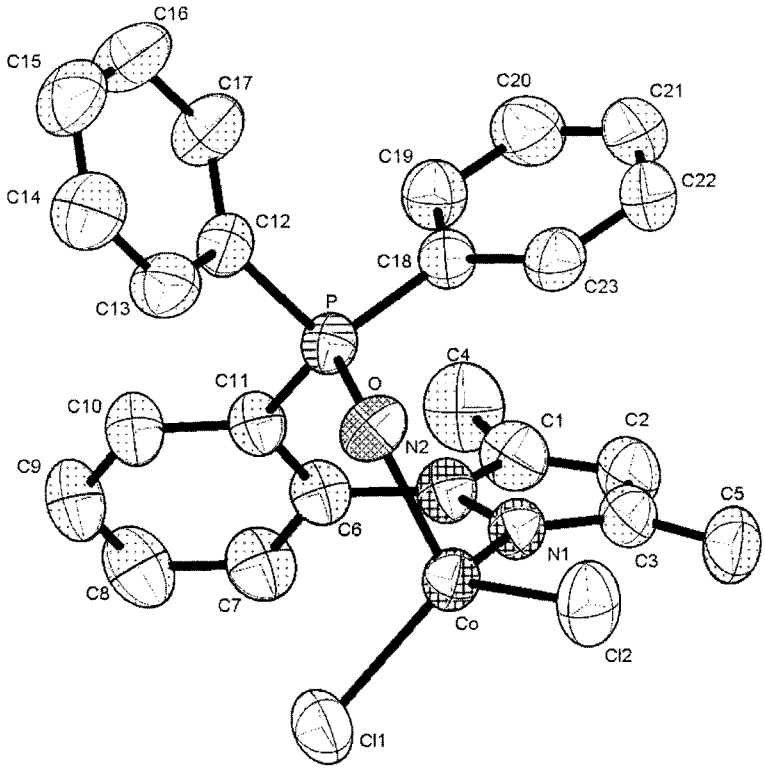


Figure 3. ORTEP diagram of complex **6**; ellipsoids drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Co–O 1.9911(11), P–O 1.5075(12), P–O–Co 121.72(6), O–Co–Cl1 112.29(4), O–Co–Cl2 103.70(4), Cl1–Co–Cl2 116.54(2).

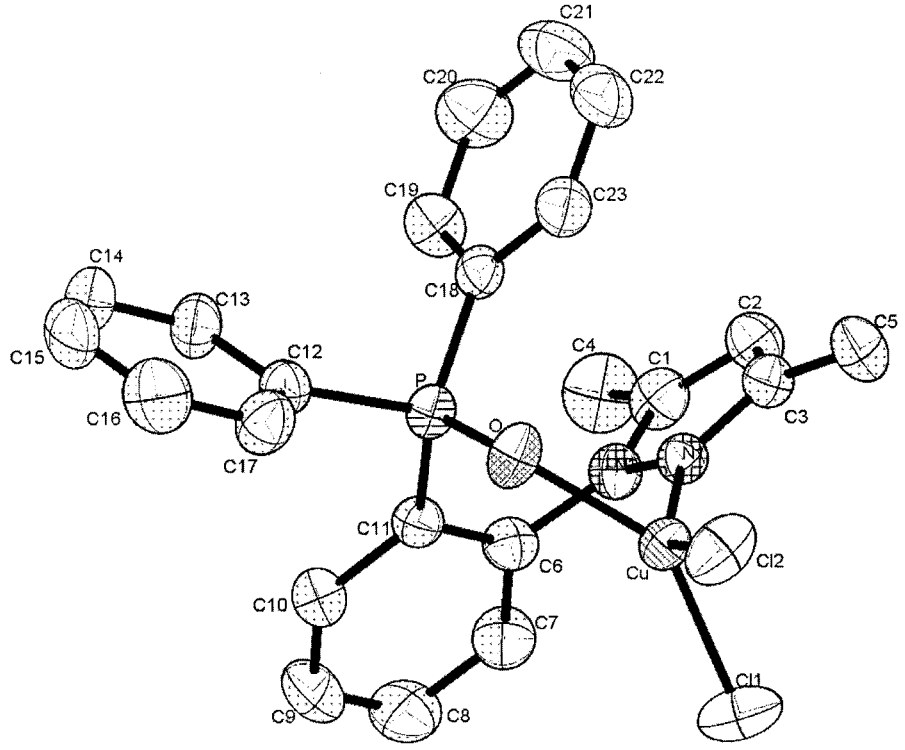


Figure 4. ORTEP diagram of complex **7**; ellipsoids drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Cu–O 1.9952(18), P–O 1.5064(18), P–O–Cu 122.40(11), O–Cu–Cl1 144.91(7), O–Cu–Cl2 93.09(6), Cl2–Cu–Cl1 100.84(3).

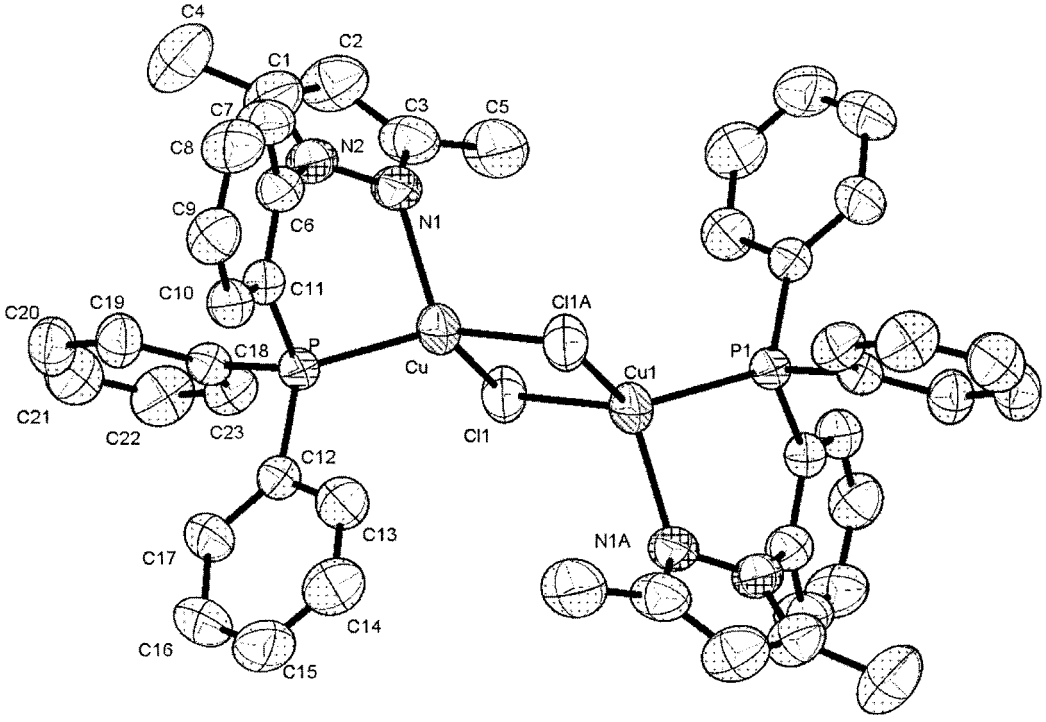


Figure 5. ORTEP diagram of complex **8**; ellipsoids drawn at 50% probability. Selected bond lengths [Å] and bond angles [°]: Cu–P 2.2205(9), Cu–Cl1 2.4140(9), Cu–Cl1A 2.4111(8), Cu–N1 2.186(2), N1–Cu–P 91.07(5), N1–Cu–Cl1 113.31(6), N1–Cu–Cl1A 111.96(7), Cl1A–Cu–Cl1 100.03(2), P–Cu–Cl1 118.83(3).

compared to 5.86 in the free ligand **2a**. Similarly, the ^{31}P NMR of **8** is at –16.37 ppm, compared with δ = –23.89 ppm for the free ligand **2a**. The relative shielding of the pyrazole-4H signal with respect to corresponding signal in the parent ligand can possibly be attributed to the π-acceptor property of pyrazole in combination with a d^{10} metal nucleus.

Since complexation was performed under argon, the oxidation of phosphane was not anticipated. Elemental analyses of complexes **6** and **7** were not consistent with the formulation of the desired phosphane complexes. After the crystal structures were determined, the presence of phosphane oxide as ligand was established beyond doubt. The observed P=O absorption bands, it was then realized, were typical of a bent M–O–P structure, which differs from that of a complex with linear M–O–P arrangement.[14]

The mechanism of oxidation by a trace amount of oxygen is probably akin to the oxidation of tributylphosphane catalyzed by Co^{II} reported earlier. Yet, the facile oxidation of triarylphosphane in this instance presents an intriguing contrast to a previous report that described difficulty in oxidizing Ph_3P by $Co(acac)_2$.[15]

The unpaired electron of such a metal center (d^7 or d^9) probably readily interacts with the paramagnetic oxygen molecules present in trace amounts to generate the reactive intermediate that eventually transfers oxygen to the phosphane.[16] Once the structures were known, the reactions were repeated in an open vessel and yields were improved considerably (up to 90%).

Complexation of $CoCl_2$ and $CuCl_2$ was repeated using fourfold an excess of the ligand **2a**. Recovered ligand showed no evidence of oxidation while the complexes indeed featured the P=O group. This suggests that these metals do not catalytically oxidize the phosphorus to phosphane oxide.

Cu^{II} coordination chemistry is dominated by N or O as donor atom followed by chlorine, bromine and sulfur. The soft donor atom P is uncommon for Cu^{II} despite its frequent occurrence in Cu^{I} coordination chemistry. In a dimeric structure, phosphane can be present as a ligand, as seen in the dinuclear complex $[Cu_2(MeCO_2)_4(PPh_3)_2]$.[17] For mononuclear complexes, this is indeed rare. Therefore, complex **7** attains stability by oxidation of the phosphane to a phosphane oxide in the presence of oxygen. To the best of our knowledge, no precedent for such an oxidation within the coordination sphere of the Cu^{II} exists. Conversely, the dimeric structure of the Cu^{I} complex **7** is unexceptional.

Ethylene Oligomerization

Several nickel or palladium complexes are efficient catalysts for the oligomerization of ethylene.[18a] The degree of branching in ethylene oligomers is an important parameter for catalyst optimization since highly branched oligomers in the C_6–C_{20} range find wide use in lubrication and other applications. Mohring and Fink reported[18b] that aminobis(imino)phosphorane nickel complexes polymerize ethylene to low molecular weight branched polyethylene. More recently, Brookhart and co-workers described a neutral, SHOP-type catalyst, featuring an anionic P–N chelating ligand,[19] that can produce branched polymers/oligomers. The synthesis and coordination behavior of new P,N ligands, therefore, continues to attract interest,[20–22] owing to the possibility of independently tuning the steric and electronic attributes of different donor groups.

Our new nickel complex **4**, featuring a chelating pyrazole ligand, is an active catalyst for ethylene oligomerization. It efficiently polymerizes ethylene under mild conditions in the presence of methylaluminoxane (MAO) to yield highly branched oligomers with a relatively narrow molecular weight distribution. Table 1 and Table 2 display the results. Nickel complexes **5a** and **5b** show no activity for ethylene polymerization in the presence of MAO.

Table 1. Oligomerization of ethylene using a nickel-based catalyst system.

Entry	Ethylene [bar]	Catalyst [mol] × 10^5	MAO [mol] × 10^2	[Al/Ni]	Temp. [°C]	Yield [mg]	TOF[a]
1	1	2.1	2.1	1000	25	600	1045
2	5	2.1	2.1	1000	25	700	1219
3	5	2.1	2.1	1000	40	800	1365
4	1	2.1	1.05	500	25	500	871

Solvent: toluene [a] TOF (turn over frequency) = mol of polymer per mol of catalyst per hour.

Table 2. Characterization of oligomers.

Entry	GPC[a]			DP	DB[b]		Branch distribution[c]				End group [mol%][d]		
	M_n	M_w	MWD	(^{1}H NMR)	^{1}H NMR	^{13}C NMR	C_1	C_2	C_3	≥ C_4	–CH=CH–	–CH=CH_2	–CH=CMe_2
1	1630	3120	1.9	40	113	134	63	16	5	48	93	5	2
2	1560	2460	1.6	33	109	136	63	19	7	49	94	3	3
3	1440	2325	1.6	36	109	132	63	17	5	45	95	3	2
4	1600	2600	1.6	39	107	130	60	14	5	51	94	4	2

[a] For GPC, polystyrene was used as standard. [b] DB (degree of branching): branches per 1000 C atoms. [c] Calculated from ^{13}C NMR spectra. [d] Calculated from ^{1}H NMR spectra.

Preliminary experiments indicate that the turnover frequency marginally increases with increasing ethylene pressure (entries 1 and 2), polymerization temperature (entries 2 and 3) and MAO concentration (entries 1 and 4).

The degree of polymerization (DP) and degree of branching were determined from the ^{1}H NMR spectrum of the oligomers following a reported method.[4a,19] The oligomers feature predominantly internal alkenes (ca. 90%), while the rest consists of 1-alkenes and some with CH_2=C(Me)C– end groups. An average of 125 branches per 1000 carbon atoms, a significant number, is estimated from the ^{1}H and ^{13}C NMR spectra (Table 2).

The average chain length of C_{60}–C_{80} and extensive branching are two noteworthy features of this new nickel catalyst. Extensive branching probably results from the 'chain running' behavior[4a] of nickel.

Conclusions

Two sets of new pyrazole-tethered bidentate ligands can form stable complexes with late transition metals such as Co^{II}, Cu^{II}, Ni^{II}, and Cu^{I}. Representative complexes were structurally characterized by crystal structure determination. For the first two metal ions, the phosphane of the ligand was readily oxidized to phosphane oxide, presumably within the metal coordination sphere. The new nickel complex activated by MAO is a highly active catalyst for ethylene oligomerization. Pyrazole-derived ligands seem to offer an alternative and viable motif for ligand design. The results are encouraging and warrant a systematic variation of donor groups and tuning of steric and electronic factors on this ligand skeleton in relation to catalytic performance and microstructure of polymer products, which is currently being pursued in our laboratory.

Experimental Section

General Procedure: All manipulations were carried out under argon. Dried solvents were used. Reagents and chemicals were used as received from Aldrich and Lancaster. M.p.s (°C) (recorded on a Thermonik Campbell melting point apparatus) are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer. NMR spectra (^{1}H, ^{13}C and ^{31}P) were recorded on Bruker AC200, MSL300 or DRX500 spectrometers. All crystal data were corrected for Lorentzian, polarization and absorption effects. SHELX-97 (ShelxTL)[24] was used for structure solution and full-matrix least-squares refinement on F^2 (see also Table 3 and Table 4). Hydrogen atoms were included in the refinement as per the riding model. CCDC-250550 (for **5b**), -250551 (for **6**), -250552 (for **7**), -250553 (for **8**) and -250554 (for **4**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Oligomerization of Ethylene: Toluene (S.D. Fine Chemicals, India) was refluxed over sodium/benzophenone and distilled under nitrogen before use. Polymerization grade ethylene was obtained from the gas cracker complex of the Indian Petrochemical Corporation, Nagothane, India. Methylaluminoxane from Witco, Germany, was used as received. NMR Spectroscopy: ^{1}H and ^{13}C NMR spectra are recorded on a high-resolution Bruker 500 MHz spectrometer. Samples were dissolved in $CDCl_3$ in 5 mm tubes at 30 °C. Quantitative ^{13}C NMR spectra were recorded with a 40° flip angle and a delay of 8 s. GC: Gas Chromatograms were obtained on a Perkin–Elmer GC 2001. The following parameters were used for analysis of oligomer. Column: Poly Wax. Operating conditions: over: 100–300 °C, ramp rate: 7 °C min^{-1}, injector: 300 °C, detector: 320 °C, carrier gas (nitrogen): 0.7 psi. GPC: molecular weight and molecular weight distribution (MWD) of the oligomers were determined using a Thermofinnigan gel permeation chromatograph equipped with a refractive index detector and μ-styraged columns (10^5 to 50 Å), based on polystyrene standards, at 25 °C using chloroform as solvent with a 1 mL min^{-1} flow rate. Data were processed using the software PSS WinGPC scientific.

Table 3. Crystal data and structure refinement of complexes **4** and **5b**.

	Complex **4**	Complex **5b**
Empirical formula	$C_{23}H_{21}Cl_2N_2NiP$	$C_{19}H_{21}Cl_2N_{3.50}Ni$
Formula mass	486.10	428.00
Temperature [K]	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/C$	monoclinic, $P2_n$
a [Å]	18.739 (2)	10.873(3)
b [Å]	10.812 (8)	12.749(4)
c [Å]	24.418 (2)	15.409(5)
β [°]	113.238(5)	109.640(5)
Volume [Å^3]	4545.9 (6)	2011.8(11)
Absorption coefficient [mm^{-1}]	1.172	1.238
$F_{(000)}$	2104	886
Crystal size [mm]	0.154 × 0.144 × 0.10	0.42 × 0.26 × 0.17
θ range for data collection (°)	1.18 to 28.20	1.60 to 28.16
Limiting indices	$-24 \le h \le 13$ $-13 \le k \le 13$ $-26 \le l \le 32$	$-14 \le h \le 13$ $-16 \le k \le 16$ $-20 \le l \le 20$
Data/restraints/parameters	10336/0/591	4735/0/243
Goodness of fit on F^2	0.860	1.059
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0575, $wR2$ = 0.1359	R1 = 0.0328, $wR2$ = 0.0864
R indices (all data)	R1 = 0.1440, $wR2$ = 0.1602	R1 = 0.0368, $wR2$ = 0.0893
Largest diff. peak and hole [e Å^{-3}]	0.504 and –0.319	0.640 and –0.341

Preparation of Ligand 2a: nBuLi (15 mL 1.41 M, 21.15 mmol) was added dropwise at 0 °C to a solution of N-phenyl-3,5-dimethylpyrazole (**1a**)[10] (3.44 g, 20 mmol) in dry THF (40 mL). The solution was, initially, yellow but changed successively to blue, yellow, and brown. The reaction mixture was then stirred for 4 to 5 h followed by addition of PPh_2Cl (3.6 mL, 20 mmol) at 0 °C. Stirring was continued for an additional 3 h. The reaction was quenched with water and extracted with ethyl acetate (40 mL × 3). The combined organic phase was dried over Na_2SO_4 and concentrated. Crude semi-solid product was purified by flash chromatography followed by crystallization to obtain **2a** as a yellowish white solid (4 g, 56%). M.p. 110 °C. IR (Nujol): 1552 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.00 (s, 3 H, CH_3), 2.19 (s, 3 H, CH_3), 5.86 (s, 1 H, PzH), 7.31 (br. s, 14 H, PhH) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 11.4, 13.2, 105.1, 127.7, 127.9, 128.1, 128.4, 129.1, 133.5, 133.9, 134.0, 135.9, 136.1, 137.4, 137.8, 139.9, 142.8, 143.2, 147.7 ppm. ^{31}P

Table 4. Crystal data and structure refinement of complexes **6**–**8**.

	Complex **6**	Complex **7**	Complex **8**
Empirical formula	$C_{23}H_{21}Cl_2CoN_2OP$	$C_{23}H_{21}Cl_2CuN_2OP$	$2[C_{23}H_{21}Cl_2CuN_2P]C_2H_3N$
Formula mass	502.25	506.86	951.87
Temperature [K]	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system, space group	triclinic, $P\bar{1}$	orthorhombic, $P2_1P2_1P2_1$	triclinic, $P\bar{1}$
a [Å]	8.987(6)	8.771(1)	9.300(3)
b [Å]	10.199(7)	13.573(2)	10.701(3)
c [Å]	12.862(9)	19.334(2)	13.859(4)
α [°]	98.303(1)	–	72.466(4)
β [°]	91.904(1)	90	71.323(4)
γ [°]	95.825(1)	–	79.023(5)
Volume [Å^3]	1159.13(14)	2301.6(5)	1239.1(6)
Z, calculated density [mg m^{-3}]	2, 1.439	4, 1.463	2, 1.331
Absorption coefficient [mm^{-1}]	1.057	1.268	1.070
$F(_{000})$	514	1036	512
Crystal size [mm]	0.39 × 0.34 × 0.09	0.31 × 0.26 × 0.21	0.80 × 0.32 × 0.21
θ range for data collection [°]	1.60–28.26	1.83–27.69	1.61–27.87
Limiting indices	$-11 \le h \le 11$ $-13 \le k \le 13$ $-16 \le l \le 16$	$-11 \le h \le 11$ $-17 \le k \le 9$ $-24 \le l \le 24$	$-11 \le h \le 12$ $-13 \le k \le 14$ $-17 \le l \le 17$
Reflections collected/ unique	13222/ 5225 [R(int) = 0.0290]	13181/ 4983 [R(int) = 0.0246]	13601/5423 [R(int) = 0.0327]
Completeness to θ	= 28.26, 91.1%	= 27.69, 95.0%	= 27.87, 91.7%
Max. and min. transmission	0.9155 and 0.6833	0.7740 and 0.6931	0.8049 and 0.4819
Refinement method	full matrix least-squares on F^2	full matrix least-squares on F^2	full matrix least-squares on F^2
Data/restraints/parameters	5225/0/273	4983/0/273	5423/0/283
Goodness-of-fit on F^2	1.055	0.955	1.077
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0331, $wR2$ = 0.0925	$R1$ = 0.0309, $wR2$ = 0.0646	$R1$ = 0.0434, $wR2$ = 0.1280
R indices (all data)	$R1$ = 0.0374, $wR2$ = 0.0950	$R1$ = 0.0369, $wR2$ = 0.0665	$R1$ = 0.0506, $wR2$ = 0.1333
Absolute structure parameter	–	–0.018(10)	–
Largest diff. peak and hole [e Å^{-3}]	0.335 and –0.281	0.433 and –0.190	1.082 and –0.384

NMR ($CDCl_3$, 81.02 MHz): δ = –23.89 ppm. $C_{23}H_{21}N_2P$ (356.40): calcd. C 77.52, H 5.89, N 7.26; found C 77.29, H 5.64, N 7.24.

Preparation of 1b: First we prepared pivaloylacetone, which on reaction with hydrazine hydrate yielded 3(5)-*tert*-butyl-5(3)-methylpyrazole.[23] Copper acetate (3.32 g, 16.62 mmol), pyridine (1.8 mL, 22.17 mmol), phenyl boronic acid (2.67 g, 22.17 mmol) and molecular sieve, dichloromethane (30 mL) were then added to the mixture of 3(5)-*tert*-butyl-5(3)-methylpyrazole (1.53 g, 11.08 mmol), and the resultant mixture was stirred for 2 days under air. Crude product was purified by column chromatography. Yield: 1.6 g (70%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.43 [s, 9 H, $C(CH_3)_3$], 2.32 (s, 3 H, CH_3), 6.12 (s,1 H, PzH), 7.36–7.48 (m, 5 H, PhH). ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 12.4, 30.5, 32.0, 103.6, 124.7, 126.9, 128.8, 138.6, 140.2, 162.0. $C_{14}H_{18}N_2$ (214.31): calcd. C 78.5, H 8.41, N 13.08; found: C 78.3, H 8.39, N 13.07.

Preparation of Ligand 2b: *n*BuLi (2.3 mL of 1.6 M, 2.55 mmol) was added dropwise to *N*-phenyl-3-*tert*-butyl-5-methylpyrazole (0.53 g, 2.48 mmol) in THF (3 mL) at 0 °C. The ice bath was removed after addition of *n*BuLi. The reaction mixture gradually changed to yellow and then brown, and stirring was continued for 6 h. PPh_2Cl (0.56 mL, 2.55 mmol) was then added at 0 °C and stirring continued for another 4 h. After the usual work up, semi-solid product was obtained that was purified by column chromatography. Yield: 0.47 g (48%); m.p. 99.5 °C. IR (neat): 1552 cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.22 [s, 9 H, $C(CH)_3$], 2.21 (s, 3 H, CH_3), 6.04 (s, 1 H, PzH), 7.29–7.46 (m, 14 H, PhH) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 11.9, 30.3, 31.8, 102.2, 127.8, 128.2, 128.5, 129.3, 133.7, 134.2, 134.7, 136.9, 137.6, 137.9, 139.3, 143.6, 144.1, 161.3 ppm. ^{31}P NMR ($CDCl_3$, 81.02 MHz): δ = –13.23 ppm. $C_{26}H_{27}N_2P$ (398.48): calcd. C 78.39, H 6.78, N 7.03; found C 78.32, H 6.67, N 6.98.

Preparation of Compound 1c: 3-Mesityl-5-methyl-*N*-phenylpyrazole (**1c**) was prepared by *N*-phenylation of 3(5)-mesityl-5(3)-methylpyrazole (0.759 g, 3.79 mmol) using phenyl boronic acid (0.918 g, 7.59 mmol) following the above procedure [copper acetate (1.14 g, 5.68 mmol), pyridine (0.61 mL, 7.59 mmol)]. Yield: 0.9 g (86%); m.p. 73–75 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.24 (s, 6 H, $2CH_3$), 2.34 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3), 6.14 (s, 1 H, PzH), 6.95 (s, 2 H, PhH), 7.03–7.58 (m, 5 H, PhH) ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ = 12.7, 20.5, 21.0, 108.1, 118.8, 122.4, 123.2, 124.5, 128.0, 128.3, 128.9, 129.7, 137.2, 137.4, 138.8, 140.0, 151.0 ppm. $C_{19}H_{20}N_2$ (276.38): calcd. C 82.60, H 7.24, N 10.14; found C 81.90, H 7.44, N 10.12.

Preparation of Ligand 2c: The lithiation procedure was the same as that mentioned above, using 3-mesityl-5-methyl-*N*-phenylpyrazole (0.2 g, 0.72 mmol), *s*BuLi (1.5 M, 0.5 mL, 0.72 mL) and PPh_2Cl: (0.13 mL, 0.72 mmol). Yield: 0.065 g (26%); m.p. 107 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.02 (s, 6 H, 2 CH_3), 2.13 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 6.04 (s, 1 H, PzH), 7.10–7.52 (m, 14 H, PhH) ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz): δ = 12.6, 20.5, 20.9, 108.1, 122.3, 124.4, 125.9, 126.0, 126.9, 127.9, 128.2, 128.4, 128.5, 128.8, 129.3, 130.8, 137.0, 137.3, 138.3, 138.7, 139.9, 140.2, 141.4, 149.2, 150.9 ppm. ^{31}P NMR ($CDCl_3$, 202.46 MHz): δ = –20.70 ppm.

$C_{31}H_{29}N_2P$ (460.55): calcd. C 80.86, H 6.30, N 6.08; found C 80.53, H 5.97, N 6.23.

Preparation of 3,5-Dimethyl-1-(2-nitrophenyl)-1*H*-pyrazole: A solution of 2-nitrophenylhydrazine (1.5 g, 9.98 mmol), one pinch of *p*-toluenesulfonic acid and acetylacetone (1.5 mL, 14.98 mmol) in dry EtOH (50–60 mL) were refluxed for 20–24 h (reaction monitored by TLC). The reaction mixture was then cooled to room temperature and the solvent was evaporated. The resultant residue was taken up in ethyl acetate and washed with aq. $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4, concentrated and purified by column chromatography using 10% acetone/petroleum ether. Yield: 2 g (62%); m.p. 178–181 °C. IR (KBr): 790, 1529, 1355 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ = 2.17 (s, 3 H, CH_3), 2.23 (s, 3 H, CH_3), 6.01 (s, 1 H, PzH), 7.45–7.59 (m, 2 H, PhH), 7.65–7.73 (m, 1 H, PhH), 7.94–7.98 (m, 1 H, PhH) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 11.2, 13.4, 106.8, 125.0, 129.3, 129.4, 132.9, 133.2, 141.0, 146.3, 150.3 ppm. $C_{11}H_{11}N_3O_2$ (217.22): calcd. C 60.82, H 5.07, N 19.35; found: C 60.11 H 5.37, N 19.18.

Preparation of 2-(3,5-Dimethylpyrazol-1-yl)phenylamine: Dry ethanol (10 mL) was added to a mixture of 3,5-dimethyl-1-(2-nitrophenyl)-1*H*-pyrazole (0.4 g, 1.84 mmol) and 10% Pd–C (45 mg) and the resultant mixture was stirred under hydrogen until the starting material was consumed (3 h, monitored by TLC). The catalyst was filtered off and the solvent was evaporated. The reaction mixture was extracted with ethyl acetate and washed with water. Subsequent removal of the solvent afforded a yellow solid. The product was pure enough to proceed to the next step. Yield: 0.28 g (70%); m.p. 75–77 °C. IR (KBr) 1629, 1550, 3207, 3315, 3413 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$) δ = 2.67 (s, 3 H, CH_3), 2.85 (s, 3 H, CH_3), 4.60 (br., 2 H, NH), 6.53 (s, 1 H, PzH), 7.24–7.31 (m, 2 H, PhH), 7.58–7.70 (m, 2 H, PhH). ^{13}C NMR (50.32 MHz, $CDCl_3$) δ = 10.9, 13.1, 105.1, 116.0, 117.2, 124.8, 127.0, 128.9, 140.2, 143.1, 148.7. $C_{11}H_{13}N_3$ (187.24): calcd. C 70.59, H 6.95, N 22.45; found C 70.27, H 6.80, N 22.42.

Preparation of [2-(3,5-Dimethylpyrazol-1-yl)phenyl]dimethylamine (Ligand 3a): Sodium cyanoborohydride (0.215 g, 3.42 mmol), and then acetic acid, were added dropwise to a solution of 2-(3,5-dimethylpyrazol-1-yl)phenylamine (0.213 g, 1.14 mmol) in acetonitrile (4 mL) and formalin (37%) (0.912 mL, 11.40 mmol). Stirring was continued for 3 h (monitored by TLC). The reaction mixture was then poured into diethyl ether (20 mL) and then washed with brine solution. The so-obtained liquid compound was purified by column chromatography. Yield: 0.161 g (66%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.06 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.46 [s, 6 H, $N(CH_3)_2$], 5.91 (s, 1 H, PzH), 6.89–6.94 (m, 2 H, PhH), 7.19–7.28 (m, 2 H, PhH) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 10.8, 13.3, 41.5, 105.0, 117.3, 120.2, 128.9, 129.4, 130.6, 140.9, 148.5. $C_{13}H_{17}N_3$ (215.29): calcd. C 72.56, H 7.91, N 19.53; found C 72.44, H 7.88, N 19.43.

Preparation of 3-Methyl-1-(2-nitrophenyl)-5-phenyl-1*H*-pyrazole: The same procedure as above was used; this time with benzoyl acetone (2 g, 12.34 mmol) and 2-nitrophenylhydrazine: (1.26 g, 8.23 mmol). Yield: 1 g (45%); m.p. 169–171 °C. IR: 765, 1350, 1527 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 6.34 (s, 1 H, PzH), 7.19–7.28 (m, 6 H, PhH), 7.30–7.52 (m, 2 H, PhH), 7.54 (d, J = 2 Hz, 1 H, PhH) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$): 13.5, 107.6, 118.3, 124.9, 128.0, 128.3, 128.4, 128.5, 129.1, 129.3, 129.4, 133.0, 133.6, 144.9, 150.9 ppm. $C_{16}H_{13}N_3O_2$ (279.29): calcd. C 68.82 H 4.65, N 19.35; found 68.37, H 4.62, N 19.18.

Preparation of 2-[3-Methyl-5-phenylpyrazol-1-yl)]phenylamine: Using the same procedure as above, 3-methyl-1-(2-nitrophenyl)-5-phenyl-1*H*-pyrazole (0.280 g) and 10% Pd/C (30 mg) were used to obtain the desired product in 96% yield (0.240 g). M.p. 73–75 °C. IR: 1504, 1635, 3209, 3321, 3450 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 3.97 (br., 1 H, NH), 6.37 (s, 1 H, PzH), 6.59–6.64 (m, 1 H, PhH), 6.79–6.85 (m, 2 H, PhH), 7.11–7.29 (m, 6 H, PhH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 13.6, 106.1, 116.7, 118.1, 128.0, 128.2, 129.1, 130.1, 142.7, 144.7, 149.8 ppm. $C_{16}H_{15}N_3$ (249.31): calcd. C 77.08, H 6.06, N 16.85; found C 77.19, H 6.14, 16.01.

Preparation of Dimethyl[2-{3-methyl-5-phenylpyrazol-1-yl)}-phenyl]amine (Ligand 3b): Ligand **3b** was prepared, by the same procedure as the previously, from 2-[3-methyl-5-phenylpyrazol-1-yl)]phenylamine (0.180 g, 0.72 mmol), $NaBH_3CN$ (0.14 g, 2.16 mmol) and formalin (7.2 mmol, 0.6 mL) in 95% yield (0.19 g). IR (neat): 1552 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 6 H, NMe_2), 2.27 (s, 3 H, CH_3), 6.21 (s, 1 H, PzH), 6.67–6.84 (m, 2 H, PhH), 6.86–7.14 (m, 6 H, PhH), 7.28–7.31 (s, 1 H, PhH) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$) δ = 13.7, 41.9, 103.8, 116.6, 122.3, 124.9, 125.0, 126.5, 127.0, 132.8, 134.5, 136.4, 154.6 ppm. $C_{18}H_{19}N_3$ (277.16): calcd. C 77.97, H 6.86, N 15.16; found C 77.85, H 6.89, N 15.13.

Preparation of Nickel Complex 4: A solution of ligand **2a** (0.356 g, 1 mmol) in acetonitrile (15 mL) was added to a yellow suspension of anhydrous $NiCl_2$ (0.128 g, 1 mmol) in acetonitrile (15 mL) at room temperature. The suspension initially turned red, and during reflux over 6–8 h a violet precipitate was formed, which was filtered off and dried under vacuum to afford violet, crystalline complex **4** (0.3 g, 62%). X-ray grade crystals were obtained from a dilute solution of the complex **4** in acetonitrile. M.p. >240 °C. $C_{23}H_{21}Cl_2N_2NiP$ (485.69): calcd. C 56.26, H 4.28, N 5.70; found C 55.74, H 4.41, N 5.41.

Preparation of Nickel Complex 5a: A solution of ligand **3a** (0.17 g, 0.8 mmol) in dichloromethane (10 mL) was added to a hazy yellow solution of $Ni(DME)Cl_2$ (0.17 g, 0.8 mmol) in dry dichloromethane (5 mL); the resultant solution immediately turned violet, and gradually changed to yellowish violet. Stirring was continued for 12 h. After removal of solvent, an orange solid was obtained, which was purified by recrystallization from hot acetonitrile. Yield: 0.199 g (82%); m.p. >240 °C. IR (Nujol): 1504, 1556 cm^{-1}. $C_{13}H_{17}Cl_2N_3Ni$ (309.2): calcd. C 50.45, H 5.49, N 13.58; found C 50.57, H 5.46, N 13.29.

Preparation of Nickel Complex 5b: A solution of **3b** (0.190 g, 0.685 mmol) in dichloromethane (10 mL) was added to a hazy yellow solution of $Ni(DME)Cl_2$ in dry dichloromethane (5 mL); immediately, the hazy yellow solution turned violet and then orange. Stirring was continued for 12 h. After removal of solvent, an orange solid was obtained that was purified by recrystallization from hot acetonitrile. Yield: 0.453 g (79%); m.p. >240 °C. IR (Nujol): 1506, 1562 cm^{-1}. $C_{36}H_{38}Cl_4N_6Ni_2 \cdot 0.5CH_3CN$ (833.9): calcd. C 53.24, H 4.74, N 10.9; found C 52.99, H 4.32, N 10.88.

Preparation of Co Complex 6: An acetonitrile solution of **2a** (0.7 g, 1.93 mmol) was added to a solution of anhydrous $CoCl_2$ (0.25 g, 1.93 mmol) in acetonitrile (10 mL); the resultant solution become deep blue and, immediately, a blue precipitate formed. After 6 h of reflux reaction, the mixture was filtered, the residue was collected and dried under vacuum to give blue solid **6** (0.5 g, 51%). X-ray quality crystals were obtained from slow evaporation of acetonitrile. When the reaction was carried out in air the yield was better (0.83 g, 84%). M.p. >240 °C. IR ($CHCl_3$): 1215, 1438, 1477 cm^{-1}. $C_{23}H_{21}Cl_2CoN_2OP$ (502.25): calcd. C 55.00, H 4.21, N 5.57; found C 55.13, H 4.21, N 5.78.

Preparation of Cu^{II} Complex 7: An acetonitrile solution (20 mL) of **2a** (0.712 g, 2 mmol) was added to a brownish yellow solution of

anhydrous $CuCl_2$ (0.27 g, 2 mmol) in acetonitrile (10 mL) at room temperature. Immediately, the solution was change color, to light yellow. It was then refluxed for 6 h; the solution turned greenish yellow. After removal of solvent, greenish compound **7** (0.42 g, 41%) was formed, which was purified by recrystallization from acetonitrile. When the reaction was performed under air the yield was improved (0.95 g, 94%). M.p. >240 °C. IR (Nujol) 1132, 1554, 1589 cm^{-1}. Microanalysis $C_{23}H_{21}Cl_2CuN_2OP$ (506.86): calcd. C 54.50, H 4.17, N 5.52; found C 54.42, H 4.32, N 5.51.

Preparation of Cu^I Complex 8: An acetonitrile solution (10 mL) of **2a** (0.356 g, 1 mmol) was added to a suspension of CuCl (0.093 g, 1 mmol) in acetonitrile (12 mL). The reaction mixture was refluxed for 12 h. The reaction slurry was filtered and the filtrate was concentrated under vacuum to give yellow solid **8** (0.40 g, 44%). Crystals suitable for X-ray analysis were obtained from an acetonitrile solution of Cu^I complex **8**. M.p. >240 °C. IR (Nujol): 1552, 1587 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ = 1.81 (s, 3 H, CH_3), 2.40 (br. s, 3 H, CH_3), 5.69 (s, 1 H, pzH), 7.24–7.54 (m, 14 H, PhH) ppm. ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 11.90, 14.00, 107.77, 128.13, 128.76, 129.20, 130.15, 131.22, 133.68, 142.02, 150.92 ppm. ^{31}P ($CDCl_3$, 80.02 MHz): δ –16.37 ppm. $C_{46}H_{42}Cl_2Cu_2N_4P_2{\cdot}CH_3CN$ (951.87): calcd. C 60.57, H 4.76, N 7.36; found C 60.46, H 4.69, N 7.02.

Ethylene Polymerization: Ethylene polymerization was performed in a 100-mL Büchi AG miniclave. Catalyst was suspended in dry toluene (30 mL) and the solvent was saturated with ethylene. Polymerization was initiated by addition of a toluene suspension of MAO. After 60 min, polymerization was terminated by the addition of methanol (5 mL). The resultant oligomeric mixture, obtained as an oil, was dried under vacuum.

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