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Ethylene and Styrene Carbon Monoxide Copolymerization Catalyzed by Pyrazolyl Palladium(II) Complexes

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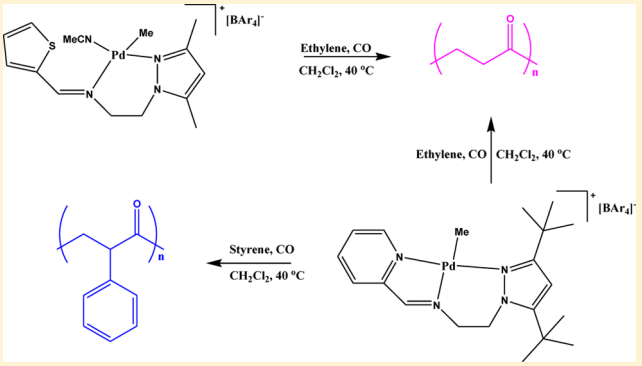
Supporting Information

ABSTRACT: The pyrazolyl pyridylimine ligands [2-(3,5-dimethylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneimine (**L1**) and [2-(3,5-di-*tert*-butylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneimine (**L2**) and pyrazolyl thienylimine ligands [2-(3,5-dimethylpyrazol-1-yl)ethyl]thiophen-2-ylmethyleneimine (**L3**), [2-(3,5-di-*tert*-butyl-pyrazol-1-yl)ethyl]thiophen-2-ylmethyleneimine (**L4**), [2-(3,5-dimethylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneimine (**L5**), and [2-(3,5-di-*tert*-butylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneimine (**L6**) were synthesized by condensation of the appropriate pyrazolylamine and the corresponding aldehyde. Reactions of **L1**−**L6** with [PdCl(Me)(cod)] gave the corresponding palladium(II) complexes [PdCl(Me)(L)] (where L = **L1** (**1a**), **L2** (**2a**), **L3** (**3a**), **L4** (**4a**), **L5** (**5a**), **L6** (**6a**)) in very good yields. The pyridylimine ligands **L1** and **L2** were found to coordinate via the imine and pyridine nitrogen atoms, while the thienylimine ligands **L3**−**L6** coordinate via imine and pyrazolyl nitrogen atoms to the palladium. The cationic complexes [Pd(Me)(A)]$^+$ (where A = **L1** (**1b**), **L2** (**2b**), **L3** (**3b**), **L4** (**4b**), **L5** (**5b**), **L6** (**6b**)) were synthesized from **1a**−**6a**, respectively, using Na[BAr$_4$] (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) in a 1:1 ratio. The cationic palladium complexes **1b** and **2b** were stabilized by the pyrazolyl nitrogen atom of ligands **L1** and **L2**, respectively, while complexes **3b**−**6b** were stabilized by NCMe. Attempts to activate **1a**−**6a** with Na[BAr$_4$] to produce active catalysts for ethylene/CO and styrene/CO led to the formation of palladium black. Using the cationic complexes **1b**−**6b**, only **2b** and **3b** were active in the copolymerization of ethylene/CO and styrene/CO.



1. INTRODUCTION

Late-transition-metal catalysts containing nitrogen-donor atoms have found applications in several polymerization reactions such as homopolymerization of olefins[1] and copolymerization of olefins/CO.[2] Palladium is the most commonly used metal to catalyze copolymerization of olefin/CO.

There have been two types of palladium catalysts developed so far for the copolymerization of olefin/CO. Both are salts of general formulas $[PdL(L')_2]^{2+}(X^-)_2$ (L = bidentate ligand, X = weakly coordinating or noncoordinating anion, L′ = coordinating solvent) and $[PdLRL']^+X^-$ (L = bidentate ligand, R = alkyl group, X = weakly coordinating or noncoordinating anion, and L′ = coordinating solvent).[2,3] These palladium(II) complexes contain a wide array of bidentate ligands, including bidentate phosphine donors (P^P), mixed phosphino-phosphite (P^O), mixed bidentate phosphorus−nitrogen (P^N) and bidentate nitrogen donors (N^N). Structural modification of the bidentate ligands and diverse structures of α-olefins, results in significant changes in reaction rate, natures of products, and molecular weights of the polyketones.[2]

The most commonly used ligand systems for the copolymerization of ethylene/CO are bisphosphines. However, the bisphosphine palladium(II) catalysts have a drawback, in that they easily degrade to inactive palladium(0) under copolymerization conditions.[4] For instance, (dppp)Pd−H$^+$ is known to be unstable in methanol and slowly undergoes deprotonation to (dppp)Pd^0, which either produces palladium(0) and the free ligand or couples with (dppp)Pd^{2+} to form the catalytically inactive binuclear species $[Pd(dppp)]_2^{2+}$,[4] although the inactive complex can be converted to catalytically active Pd−H or Pd−OMe species by the addition of an oxidant such as 1,4-benzoquinone. Furthermore, the use of bisphosphine palladium complexes is limited to either ethylene/CO or aliphatic α-olefin/CO copolymerization. For

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instance, when styrene is used, only short-chain oligomers are produced. As a result of these drawbacks, nitrogen-based catalysts are becoming the preferred choice especially for styrene/CO copolymerizations.

Over the past 10 years a variety of bidentate nitrogen-donor metal complexes have been used as olefin/CO copolymerization catalysts. Examples range from 2,2-bipyridine,[5] 1,10-phenanthroline,[6] oxazoline base,[7] and α-diimine[8] to pyrazoles.[9] Incorporation of pyrazole in ligands is gaining ground due to (i) the weaker donor ability of pyrazoles compared to other nitrogen donors such as imines and pyridines that can render metal centers in such pyrazolyl catalyst systems more electrophilic and (ii) the ability to easily modify electronic and steric properties of the catalysts, by adding different substituents on the pyrazolyl unit. A recent review of pyrazolyl metal complexes as catalysts for various carbon−carbon coupling reactions[10] demonstrate the extent to which the above two properties of pyrazolyl metal complexes manifest themselves in olefin/CO copolymerization and other areas of catalysis.

There have been few reports on the use of terdentate nitrogen-donor ligands in olefin/CO copolymerization catalysis.[11] Most of the reports are on the mechanistic studies. Examples are terdentate nitrogen-donor ligands 2,2′:6′,2″-terpyridine (terpy), 2,6-bis(2-pyrimidyl)pyridine, and 2,6-bis-(*N*-pyrazolyl)pyridine.[11b,12,13] An exception is a recent report by Milani and co-workers,[7b] where the terdentate ligand 2-oxazolinylphenanthroline is used as a support for a palladium catalyst in styrene/CO copolymerization.

Here we report the synthesis of two classes of new terdentate pyrazolyl ligands: one with a pyridinylimine group (**L1** and **L2**) and the other with a thienylimine group (**L3**−**L6**), their methylpalladium chloride complexes (**1a**−**6a**), their cationic palladium complexes (**1b**−**6b**), and application of these pyrazolyl palladium complexes as catalysts for ethylene/CO and styrene/CO copolymerizations.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods. Unless otherwise stated, all manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. Polymerization was carried out using a 50 mL stainless steel autoclave. All organic solvents were dried and purified by distillation over standard reagents under argon prior to use. The compounds [PdClMe(cod)][13] and alkylpyrazolylamine[14] were synthesized according to literature procedures. The compounds 3,5-dimethylpyrazole, 2-bromoethylamine hydrochloride, thiophene-2-carboxaldehyde, 5-bromothiophene-2-carboxaldehyde, pyridine-2-carboxaldehyde, 2,2,6,6-tetramethyl-3,5-heptadione, styrene, and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP; *caution*! HFIP is a very toxic compound) were purchased from Sigma-Aldrich while Na[BAr_4] (Ar = 3,5-$(CF_3)_2C_6H_3$) was purchased from Boulder Chemicals; all chemicals were used as received.

Infrared (IR) spectra of ligands and complexes were recorded on a Bruker Tensor 27 equipped with a Diamond ATR. Elemental analyses were performed on a Vario Elementar III Microcube CHNS analyzer at Rhodes University. The mass spectrometry unit at the University of Stellenbosch performed the ESI-MS spectra on a Waters API Qualtro micro spectrophotometer. NMR spectra were recorded on a Bruker 400 MHz instrument (^{1}H at 400 MHz and ^{13}C{^{1}H} at 100 MHz). The chemical shifts are reported in δ (ppm) and referenced to the residual proton and carbon signals at 7.24 and 77.0 ppm, respectively, of $CDCl_3$ NMR solvent.

NMR spectroscopy data for copolymers were recorded on a JEOL JNM-ECS 400 instrument, which has ^{1}H at 400 MHz and ^{13}C{^{1}H} at 101 MHz with digital resolutions of 0.11 and 0.96 Hz, respectively. Chemical shifts for ^{1}H NMR spectra are reported in δ (ppm) downfield from tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra for copolymers were recorded on a Shimadzu FTIR-8400 spectrometer with a KBr plate. Size exclusion chromatography (SEC) analyses were carried out at 40 °C with polystyrene as internal standard, equipped with a GL Sciences instrument (Model PU 610 high-performance liquid chromatography pump, CO 631 liquid chromatography column oven, and RI 713 refractive-index detector) and with two columns (Shodex KF-804 L). The columns were eluted with tetrahydrofuran (THF) at a rate of 1 mL min^{-1}. Differential scanning calorimetry (DSC) measurements were performed on a Seiko DSC 7020 analyzer at a heating and cooling rate of 10 °C min^{-1}, and the reported T_g values were determined during the cooling process. Thermogravimetric analyses (TGA) were performed on a Seiko EXSTAR 6000 TG/DTA 6200 analyzer at a heating rate of 10 °C min^{-1}.

2.2. Syntheses of Ligands and Complexes. *2.2.1. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneimine (**L1**).* An EtOH solution (20 mL) of pyridine-2-carboxaldehyde (1.08 g, 0.01 mol) was added to a stirred EtOH solution (30 mL) of 3,5-dimethylpyrazolylamine (1.40 g, 0.01 mol). The resulting mixture was refluxed at 60 °C for 12 h to give an orange solution. This solution was filtered, and the filtrate was evaporated. The orange sticky product was redissolved in CH_2Cl_2, and the undissolved solid was filtered off. The filtrate was evaporated, and the crude product was purified by sublimation, affording **L1** as a dark orange oil. Yield: 1.41 g (62%). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 3H, CH_3); 2.18 (s, 3H, CH_3); 4.06 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 4.32 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 5.67 (s, 1H, pz-H); 7.31 (t, 1H, $^3J_{HH}$ = 6.0 Hz, 2-py-H); 7.74 (t, 1H, $^3J_{HH}$ = 6.0 Hz, 3-py-H); 7.89 (d, 1H, $^3J_{HH}$ = 8.1 Hz, 4-py-H); 8.12 (s, 1H, CH═N); 8.61 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-py-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5; 15.2; 63.3; 65.1; 108.3; 125.1; 127.5; 139.5; 145.9; 151.3; 155.1; 162.6; 167.7. IR (Diamond ATR, cm^{-1}): 1649 ν(CH═N) imine. HRMS (ESI): $[M + H]^+$ m/z 229.1450 (100%).

Compounds **L2**−**L6** were prepared following the same procedure as described for compound **L1**, using the appropriate reagents.

*2.2.2. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneimine (**L2**).* Pyridine-2-carboxaldehyde (0.09 g, 0.84 mmol) was reacted with 3,5-di-*tert*-butylpyrazolylamine (0.18 g, 0.84 mmol) to give a light yellow oily material, which solidified after 1 week. Yield: 0.15 g (75%). ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H, ^{t}Bu); 1.33 (s, 9H, ^{t}Bu); 4.19 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 4.50 (t, 2H, $^3J_{HH}$ = 6.6 Hz, CH_2); 5.72 (s, 1H, pz-H); 7.30 (t, 1H, $^3J_{HH}$ = 6.3 Hz, 2-py-H); 7.72 (t, 1H, $^3J_{HH}$ = 7.2, Hz 3-py-H); 7.89 (d, 1H, $^3J_{HH}$ = 7.5 Hz, 4-py-H); 8.27 (s, 1H, CH═N); 8.62 (d, 1H, $^3J_{HH}$ = 6.0 Hz, 1-py-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.3; 33.3; 33.7; 38.1; 64.3; 65.7; 108.7; 126.5; 128.8; 139.9; 146.9; 153.4; 156.6; 164.1; 168.3. IR (Diamond ATR, cm^{-1}): 1644 ν(CH═N) imine. HRMS (ESI): $[M + H]^+$ m/z 313.2350 (100%).

*2.2.3. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]thiophen-2-ylmethyleneimine (**L3**).* Thiophene-2-carboxaldehyde (0.81 g, 7.26 mmol) was reacted with 3,5-dimethylpyrazolylamine (1.01 g, 7.26 mmol) to give a dark purple oil. Yield: 1.35 g (80%). ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H, CH_3); 2.18 (s, 3H, CH_3); 3.94 (t, 2H, $^3J_{HH}$ = 5.6 Hz, CH_2); 4.26 (t, 2H, $^3J_{HH}$ = 5.6 Hz, CH_2); 5.64 (s, 1H, pz-H); 7.02 (t, 1H, $^3J_{HH}$ = 3.6 Hz, 2-th-H); 7.17 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 3-th-H); 7.36 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H); 7.97 (s, 1H, CH═N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.5; 13.1; 51.3; 53.6; 106.9; 126.9; 128.0; 130.8; 137.9; 139.7; 149.5; 152.5. IR (Diamond ATR, cm^{-1}): 1633 ν(CH═N) imine. HRMS (ESI): $[M + H]^+$ m/z 234.0082 (100%).

*2.2.4. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]-thiophen-2-ylmethyleneimine (**L4**).* Thiophene-2-carboxaldehyde (0.51 g, 4.57 mmol) was reacted with 3,5-di-*tert*-butylpyrazolylamine (1.02 g, 4.57 mmol) to give a yellow oil material, which solidified after 1 week at room temperature. Yield: 1.18 g (82%). ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 9H, ^{t}Bu); 1.30 (s, 9H, ^{t}Bu); 4.11 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 4.42 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 5.69 (s, 1H, pz-H); 7.01 (t, 1H, $^3J_{HH}$ = 3.6 Hz, 2-th-H); 7.15 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 3-th-H); 7.34 (d, 1H, $^3J_{HH}$ = 5.2 Hz, 1-th-H); 8.09 (s, 1H, CH═N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.4; 33.1; 33.5; 37.7; 47.8; 59.5; 105.5; 127.2; 134.5;

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136.9; 138.4; 139.9; 150.2; 164.2. IR (Diamond ATR, cm^{-1}): 1635 ν(CH=N) imine. HRMS (ESI): $[M + H]^+$ m/z 318.2004 (100%).

*2.2.5. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneimine (**L5**).* 5-Bromothiophene-2-carboxaldehyde (0.96 g, 5.00 mmol) was reacted with 3,5-dimethylpyrazolylamine (0.69 g, 5.00 mmol) to give a dark purple oil. Yield: 1.25 g (80%). ^{1}H NMR ($CDCl_3$): δ 2.15 (s, 3H, CH_3); 2.17 (s, 3H, CH_3); 3.90 (t, 2H, $^3J_{HH}$ = 5.6 Hz, CH_2); 4.24 (t, 2H, $^3J_{HH}$ = 5.6 Hz, CH_2); 5.65 (s, 1H, pz-H); 6.89 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 3-th-H); 6.97 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 2-th-H); 7.82 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.9; 13.7; 51.6; 54.1; 105.2; 127.1; 127.2; 131.2; 136.5; 137.1; 147.1; 151.3. IR (Diamond ATR, cm^{-1}): 1632 ν(CH=N) imine. HRMS (ESI): $[M - H]^+$ m/z 310.2019 (40%), $[M - Br]^+$ m/z 231.1604 (100%).

*2.2.6. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneimine (**L6**).* 5-Bromothiophene-2-carboxaldehyde (0.87 g, 4.57 mmol) was reacted with 3,5-di-*tert*-butylpyrazolylamine (1.02 g, 4.57 mmol) to give a yellow oil, which solidified after 1 week at room temperature. Yield: 1.48 g (82%). ^{1}H NMR ($CDCl_3$): δ 1.28 (s, 9H, ^{t}Bu); 1.30 (s, 9H, ^{t}Bu); 4.08 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 4.40 (t, 2H, $^3J_{HH}$ = 6.0 Hz, CH_2); 5.69 (s, 1H, pz-H); 6.86 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 3-th-H); 6.96 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 2-th-H); 7.93 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 31.2 ; 33.2; 33.5; 37.9; 47.5; 58.2; 105.2; 125.1; 133.4; 134.1; 138.2; 138.9; 149.1; 162.5. IR (Diamond ATR, cm^{-1}): 1632 ν(CH=N) imine. HRMS (ESI): $[M + 2H]^+$ m/z 398.1072 (40%), $[M - Br]^+$ m/z 316.2032 (100%).

*2.2.7. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneiminemethylpalladium(II) Chloride (**1a**).* A Et_2O solution (20 mL) of **L1** (0.98 g, 4.33 mmol) was added to a suspension of [PdCl(Me)(cod)] (1.15 g, 4.33 mmol) in Et_2O (10 mL) with stirring. The resulting suspension was stirred for 12 h at 25 °C. The reaction mixture was filtered, and the solid was isolated, washed three times with 20 mL of Et_2O, and dried in air to give an analytically pure yellow powder of **1**. Yield: 1.17 g (70%). ^{1}H NMR ($CDCl_3$): δ 1.00 (s, 3H, Pd-CH_3); 2.19 (s, 3H, CH_3); 2.36 (s, 3H, CH_3); 5.59 (s, 1H, pz-H); 4.23 (t, 2H, $^3J_{HH}$ = 5.2 Hz, CH_2); 4.28 (t, 2H, $^3J_{HH}$ = 5.2 Hz, CH_2); 7.41 (t, 1H, $^3J_{HH}$ = 7.6 Hz, 2-py-H); 7.46 (s, 1H, CH=N) 7.62 (t, 1H, $^3J_{HH}$ = 5.2 Hz, 3-py-H); 7.93 (d, 1H, $^3J_{HH}$ = 7.6 Hz, 4-py-H); 9.02 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-py-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.4; 13.5; 15.2; 47.19; 59.19; 104.8; 125.5; 128.2; 138.7; 141.1; 148.7; 149.4; 151.2; 168.5. IR (Diamond ATR, cm^{-1}): 1589 ν(CH=N) imine. Anal. Calcd for $C_{19}H_{28}Cl_2N_4Pd$: C, 43.65; H, 4.97; N, 14.54. Found: C, 44.10; H, 4.80; N, 14.37.

Complexes **2a**−**6a** were prepared following the same procedure as described for complex **1a**, using the appropriate reagents.

*2.2.8. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneiminemethylpalladium(II) Chloride (**2a**).* Compound **L2** (0.31 g, 1.00 mmol) was reacted with [PdCl(Me)(cod)] (0.27 g, 1.00 mmol) to give **2** as a yellow solid. Yield: 0.35 g (75%). ^{1}H NMR ($CDCl_3$): δ 0.99 (s, 3H, Pd-CH_3); 1.26 (s, 9H, ^{t}Bu); 1.29 (s, 9H, ^{t}Bu); 4.45 (d, 2H, $^3J_{HH}$ = 4.0 Hz, CH_2); 4.60 (d, 2H, $^3J_{HH}$ = 4.0 Hz, CH_2); 5.72 (s, 1H, pz-H); 7.36 (t, 1H, $^3J_{HH}$ = 5.2 Hz, 2-py-H); 7.59 (t, 1H, $^3J_{HH}$ = 7.6 Hz, 3-py-H); 7.87 (s, 1H, CH=N); 8.55 (d, 1H, $^3J_{HH}$ = 5.2 Hz, 4-py-H); 9.00 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-py-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.9; 29.4; 37.2; 36.5; 49.3; 58.51; 105.2; 127.9; 130.1; 139.7; 144.51; 150.8; 151.4; 153.2; 169.5. IR (Diamond ATR, cm^{-1}): 1592 ν(CH=N) imine. Anal. Calcd for $C_{20}H_{31}ClN_4Pd$: C, 50.77; H, 6.73; N, 12.02. Found: C, 51.18; H, 6.66; N, 11.94.

*2.2.9. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]thiophen-2-ylmethyleneiminemethylpalladium(II) Chloride (**3a**).* Compound **L3** (0.10 g, 0.43 mmol) was reacted with [PdCl(Me)(cod)] (0.11 g, 0.43 mmol) to give **3a** as a violet solid. Yield: 0.14 g (80%). ^{1}H NMR ($CDCl_3$): δ 0.70 (s, 3H, Pd-CH_3); 0.93 (s, 3H, Pd-CH_3) 2.18 (s, 3H, CH_3); 2.26 (s, 3H, CH_3); 2.36 (s, 3H, CH_3); 5.68 (s, 1H, pz-H); 5.80 (s, 1H, pz-H_{iso}); 7.05 (t, 1H, $^3J_{HH}$ = 4.0 Hz, 2-th-H_{iso}); 7.11 (t, 1H, $^3J_{HH}$ = 4.4 Hz, 2-th-H); 7.56 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 3-th-H_{iso}); 7.58 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 3-th-H); 7.65 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H_{iso}); 7.74 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H); 8.23 (s, 1H, CH=N_{iso}); 8.32 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.0; 11.8; 13.1; 46.8; 60.4; 105.9; 126.9; 134.0; 136.8; 137.9; 139.7; 149.5; 162.5. IR (Diamond ATR, cm^{-1}): 1622 ν(CH=N) imine. Anal. Calcd for $C_{13}H_{18}ClN_3PdS$: C, 40.01; H, 4.65; N, 10.77; S, 8.20. Found: C, 40.05; H, 4.75; N, 10.48; S, 7.74.

*2.2.10. Synthesis of [2-(3,5-Di-tert-butyl-pyrazol-1-yl)ethyl]-thiophen-2-ylmethyleneiminemethylpalladium(II) Chloride (**4a**).* Compound **L4** (0.14 g, 0.44 mmol) was reacted with [PdCl(Me)-(cod)] (0.12 g, 0.44 mmol) to give **4a** as a light orange solid. Yield: 0.16 g (82%). ^{1}H NMR ($CDCl_3$): δ 0.87 (s, 3H, Pd-CH_3); 1.33 (s, 9H, ^{t}Bu); 1.45 (s, 9H, ^{t}Bu); 5.76 (s, 1H, pz-H); 7.11 (t, 1H, $^3J_{HH}$ = 4.4 Hz, 2-th-H); 7.69 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 3-th-H); 7.72 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H); 8.32 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 10.1; 28.5; 29.1; 30.0; 32.0; 45.1; 49.3; 135.5; 138.5; 148.1; 164.2. IR (Diamond ATR, cm^{-1}): 1620 ν(CH=N) imine. Anal. Calcd for $C_{19}H_{30}ClN_3PdS$: C, 48.10; H, 6.37; N, 8.86; S, 6.74. Found: C, 48.13; H, 6.66; N, 8.66; S, 6.40.

*2.2.11. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneiminemethylpalladium(II) Chloride (**5a**).* Compound **L5** (0.14 g, 0.43 mmol) was reacted with [PdCl(Me)-(cod)] (0.11 g, 0.43 mmol) to give **5a** as a light brown solid. Yield: 0.16 g (80%). ^{1}H NMR ($CDCl_3$): δ 0.73 (s, 3H, Pd-CH_3); 0.94 (s, 3H, Pd-CH_{3iso}); 2.18 (s, 3H, CH_3); 2.26 (s, 3H, CH_{3iso}); 2.27 (s, 3H, CH_{3iso}); 2.36 (s, 3H, CH_3); 5.69 (s, 1H, pz-H); 5.81 (s, 1H, pz-H_{iso}); 7.01 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 2-th-H_{iso}); 7.07 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 2-th-H) 7.29 (d, 1H, $^3J_{HH}$ = 2.0 Hz, 3-th-H); 8.10 (s, 1H, CH=N_{iso}); 8.18 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.0; 11.56; 13.0; 47.9; 58.9; 107.1; 125.5; 131.6; 137.8; 138.1; 139.3; 149.1; 160.0. IR (Diamond ATR, cm^{-1}): 1626 ν(CH=N) imine. Anal. Calcd for $C_{13}H_{17}BrClN_3PdS$: C, 33.28; H, 3.65; N, 8.95; S, 6.82. Found: C, 33.24, H, 3.13; N, 7.87; S, 6.72.

*2.2.12. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneiminemethylpalladium(II) Chloride (**6a**).* Compound **L6** (0.17 g, 0.44 mmol) was reacted with [PdCl(Me)(cod)] (0.12 g, 0.44 mmol) to give **6a** as a light brown solid. Yield: 0.20 g (82%). ^{1}H NMR ($CDCl_3$): δ 0.88 (s, 3H, Pd-CH_3); 1.33 (s, 3H, ^{t}Bu); 1.46 (s, 3H, ^{t}Bu); 5.77 (s, 1H, pz-H); 7.07 (d, 1H, $^2J_{HH}$ = 4.0 Hz, 2-th-H); 7.35 (d, 1H, $^2J_{HH}$ = 3.2 Hz, 3-th-H); 8.20 (s, 1H, CH=N). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 9.1; 29.1; 29.8; 30.4; 31.6; 45.1; 49.3; 121.5; 135.1; 146.2; 163.1. IR (Diamond ATR, cm^{-1}): 1619 ν(CH=N) imine. Anal. Calcd for $C_{19}H_{29}BrClN_3PdS$: C, 41.24; H, 5.28; N, 7.59; S, 5.78. Found: C, 41.36; H, 5.20; N, 7.21; S, 6.11.

*2.2.13. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]pyridin-2-ylmethyleneiminemethylpalladium(II) Tetrakis(3,5-trifluoromethylphenyl)borate (**1b**).* A CH_2Cl_2 (20 mL) of complex **1a** (0.07 g, 0.18 mmol) was added to an NCMe solution (10 mL) of Na[BAr_4] (0.16 g, 0.18 mmol). The resulting mixture was stirred at 25 °C for 2 h to afford a light yellow mixture, which was filtered through a plug of Celite, and the filtrate was evaporated in vacuo to give an oily material. The oily material was dried under high vacuum overnight, after which a foamy light orange solid formed. Yield: 0.21 g (97%). ^{1}H NMR ($CDCl_3$): δ 1.04 (s, 3H, Pd-CH_3); 2.28 (s, 6H, CH_3); 3.65 (t, 2H, $^3J_{HH}$ = 5.2 Hz, CH_2); 4.30 (t, 2H, $^3J_{HH}$ = 5.2 Hz, CH_2); 6.03 (s, 1H, pz-H); 7.39 (d, 1H, $^3J_{HH}$ = 7.6 Hz, 2-py-H); 7.49 (s, 4H, BAr_4); 7.69 (s, 8H, BAr_4); 7.94 (s, 1H, CH=N); 7.97 (t, 1H, $^3J_{HH}$ = 8.0 Hz, 3-py-H); 8.50 (d, 1H, $^3J_{HH}$ = 5.2 Hz, 1-py-H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 2.1; 11.7; 14.7; 48.3; 55.8; 108.8; 117.5; 120.4; 123.1; 125.8; 127.6; 128.9; 134.7; 140.1; 143.0; 149.7; 153.0; 155.0; 162.4. IR (Diamond ATR, cm^{-1}): 1609 ν(CH=N) imine. Anal. Calcd for $C_{46}H_{31}N_4PdBF_{24}$: C, 45.50; H, 2.55; N, 4.61. Found: C, 46.01; H, 2.55; N, 4.64. Positive ion ESI-MS: m/z (%) = 349.1 (100%) $[M]^+$. Negative ion ESI-MS: m/z (%) 863.0 (100%) $[M]^-$.

Complexes **2b**−**6b** were prepared in a manner similar to that described for **1b**.

*2.2.14. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]-pyridin-2-ylmethyleneiminemethylpalladium(II) Tetrakis(3,5-trifluoromethylphenyl)borate (**2b**).* Complex **2a** (0.07 g, 0.16 mmol) was reacted with NCMe and Na[BAr_4] (0.14 g, 0.16 mmol) to give **2b** as a light orange solid. Yield: 0.19 g (90%). ^{1}H NMR ($CDCl_3$): δ 1.11 (s, 3H, Pd-CH_3); 1.37 (s, 8H, ^{t}Bu); 1.51 (s, 8H, ^{t}Bu); 3.56 (t, 1H, $^2J_{HH}$ = 11.7 Hz, CH_2); 3.76 (d, 1H, $^2J_{HH}$ = 10.5 Hz, CH_2);

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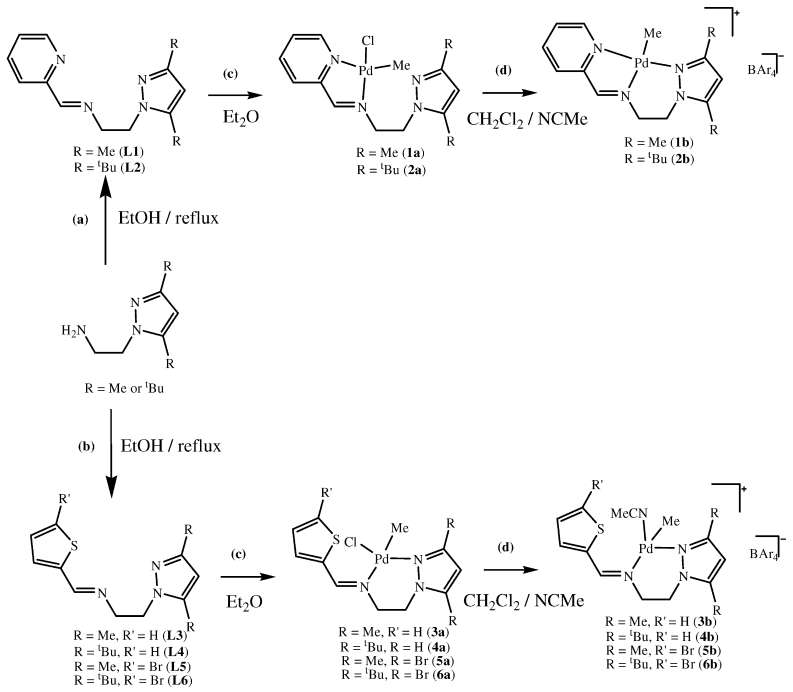
Scheme 1. Syntheses of Pyrazolylimine Ligands and Their Palladium Complexes[a]



[a]Reagents: (a) pyridine-2-carboxaldehyde; (b) thiophene-2-carboxaldehyde; (c) [PdCl(Me)(cod)]; (d) Na[BAr_4].

4.67 (t, 1H, $^2J_{HH}$ =10.5 Hz, CH_2); 4.68 (d, 1H, $^2J_{HH}$ = 15.3 Hz, CH_2); 6.15 (s, 1H, pz-H); 7.35 (d, 1H, $^3J_{HH}$ = 7.6 Hz, 2-py-H); 7.48 (s, 4H, BAr_4); 7.62 (t, 1H, $^3J_{HH}$ = 6.4 Hz, 3-py-H); 7.89 (s, 8H, BAr_4); 7.92 (t, 1H, $^3J_{HH}$ = 8.0 Hz, 4-py-H); 7.97 (s, 1H, CH═N); 8.50 (d, 1H, $^3J_{HH}$ = 5.2 Hz, 1-py-H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 3.1; 32.1; 33.4; 33.8; 37.0; 49.5; 57.1; 109.4; 119.2; 125.1; 124.5; 124.9; 128.3; 130.0; 135.1; 143.8; 144.3; 150.0; 154.2; 156.1; 169.1. IR (Diamond ATR, cm^{-1}): 1627 ν(CH═N) imine. Anal. Calcd for $C_{52}H_{43}N_4PdBF_{24}$: C, 48.10; H, 3.31; N, 4.31. Found: C, 47.73; H, 3.59; N, 4.44. Positive ion ESI-MS: m/z (%) 433.0 (100%) [M]. Negative ion ESI-MS: m/z (%) 863.0 (100%) $[M]^-$.

*2.2.15. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]thiophen-2-ylmethyleneiminemethylpalladium(II) Tetrakis(3,5-trifluoromethylphenyl)borate (**3b**).* Complex **3a** (0.20 g, 0.52 mmol) was added to an NCMe solution of Na[BAr_4] (0.46 g, 0.52 mmol) to give **3b** as a light orange solid product. Yield: 0.61 g (93%). ^1H NMR ($CDCl_3$): δ 0.70 (s, 3H, Pd-CH_3); 0.94 (s, 3H, Pd-CH_{3iso}); 2.04 (s, 6H, CH_{3iso}); 2.11 (s, 3H, CH_3); 2.19 (s, 3H, CH_3); 2.25 (s, 3H, Pd-NC-CH_3); 3.63 (t, 1H, $^2J_{HH}$ = 10.0 Hz, CH_2); 4.30 (m, 2H, CH_2); 5.39 (t, 1H, $^3J_{HH}$ = 4.0 Hz, CH_2); 5.72 (s, 1H, pz-H); 5.84 (s, 1H, pz-H_{iso}); 7.07 (t, 1H, $^3J_{HH}$ = 4.0 Hz, 2-th-H); 7.13 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 2-th-H_{iso}); 7.37 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 3-th-H); 7.48 (s, 4H, BAr_4); 7.60 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 4-th-H_{iso}); 7.69 (s, 8H, BAr_4); 7.76 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H); 7.87 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H_{iso}); 8.00 (s, 1H, CH═N); 8.19 (s, 1H, CH═N_{iso}). IR (Diamond ATR, cm^{-1}): 1623 ν(CH═N) imine. Anal. Calcd for $C_{47}H_{33}N_4PdSBF_{24}$: C, 44.79: H, 2.62; N, 4.45; S, 2.54. Found: C, 44.13; H, 2.21; N, 4.21; S, 3.33. Positive ion ESI-MS: m/z (%) 354.0 (10%) $[M - NCMe]^+$, 380.0 (10%) $[M - Me]^+$. Negative ion ESI-MS: m/z (%) 863.0 (100%) $[M]^-$.

*2.2.16. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]-thiophen-2-ylmethyleneiminemethylpalladium(II) Tetrakis(3,5-trifluoromethylphenyl)borate (**4b**).* Complex **4a** (0.06 g, 0.13 mmol) and Na[BAr_4] (0.12 g, 0.13 mmol) were reacted to give **4b** as a foamy orange solid. Yield: 0.17 g (95%). ^1H NMR ($CDCl_3$): δ 0.85 (s, 3H, Pd-CH_3); 1.30 (s, 18H, ^{t}Bu); 2.22 (s, 3H, Pd-NC-CH_3); 5.86 (s, 1H, pz-H); 7.15 (t, 1H, $^3J_{HH}$ = 4.4 Hz, 2-th-H); 7.49 (s, 4H, BAr_4); 7.55 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 3-th-H); 7.67 (s, 8H, BAr_4); 7.78 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 1-th-H); 8.23 (s, 1H, CH═N). IR (Diamond ATR, cm^{-1}): 1627 ν(CH═N) imine. Anal. Calcd for $C_{53}H_{45}N_4PdSBF_{24}$: C, 47.35; H, 3.35; N, 4.17; S, 2.38. Found: C, 47.42; H, 3.33; N, 4.09; S, 2.75. Positive ion ESI-MS: m/z (%) 423.0 (15%) $[M - Me - NCMe]^+$. Negative ion ESI-MS: m/z (%) 863.0 (100%) $[M]^-$.

*2.2.17. Synthesis of [2-(3,5-Dimethylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneiminemethylpalladium(II) Tetrakis(3,5-trifluoromethylphenyl)borate (**5b**).* Complex **5a** (0.12 g, 0.27 mmol) was reacted with Na[BAr_4] (0.24 g, 0.27 mmol) to afford **5b** as an orange solid product. Yield: 0.33 g (90%). ^1H NMR ($CDCl_3$): δ 0.70 (s, 3H, Pd-CH_3); 0.94 (s, 3H, Pd-CH_{3iso}); 2.04 (s, 6H, CH_{3iso}); 2.11 (s, 3H, CH_3); 2.19 (s, 3H, CH_3); 2.27 (s, 3H, Pd-NC-CH_3); 3.63 (t, 1H, $^2J_{HH}$ = 10.0 Hz, CH_2); 4.24 (t, 1H, $^3J_{HH}$ = 4.8 Hz CH_2); 4.30 (t, 1H, $^2J_{HH}$ = 11.6 Hz, CH_2); 5.39 (t, 1H, $^3J_{HH}$ = 4.0 Hz, CH_2); 5.72 (s, 1H, pz-H); 5.84 (s, 1H, pz-H_{iso}); 7.07 (d, 1H, $^3J_{HH}$ = 4.8 Hz, 2-th-H_{iso}); 7.13 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 2-th-H); 7.37 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 3-th-H_{iso}); 7.48 (s, 4H, BAr_4); 7.60 (d, 1H, $^3J_{HH}$ = 3.2 Hz, 3-th-H); 7.69 (s, 8H, BAr_4); 8.00 (s, 1H, CH═N); 8.19 (s, 1H, CH═N_{iso}). IR (Diamond ATR, cm^{-1}): 1620 ν(CH═N) imine. Anal. Calcd for $C_{47}H_{32}BrN_4PdSBF_{24}$: C, 40.47; H, 2.38; N, 3.93; S, 2.24. Found: C, 40.04, H, 2.04; N, 3.40%; S, 2.82. Positive ion ESI-MS: m/z (%) 433.0 (18%) $[M - NCMe]^+$, 460.0 (10%) $[M - Me]^+$. Negative ion ESI-MS: m/z (%) 863.0 (100%) $[M]^-$.

*2.2.18. Synthesis of [2-(3,5-Di-tert-butylpyrazol-1-yl)ethyl]-2-bromothiophen-2-ylmethyleneiminemethylpalladium(II) Tetrakis-(3,5-trifluoromethylphenyl)borate (**6b**).* Complex **6a** (0.23 g, 0.42 mmol) was reacted with Na[BAr_4] (0.37 g, 0.42 mmol) to afford **6b** as a foamy light orange solid. Yield: 0.54 g (90%). ^1H NMR ($CDCl_3$): δ 0.88 (s, 3H, Pd-CH_3); 1.28 (s, 9H, ^{t}Bu); 1.31 (s, 9H, ^{t}Bu); 2.24 (s, 3H, Pd-NC-CH_3); 3.63 (t, 1H,$^2J_{HH}$ =11.6 Hz, CH_2); 4.16 (d, 1H, $^2J_{HH}$ = 13.6 Hz, CH_2); 4.74 (d, 1H, $^2J_{HH}$ =15.2 Hz, CH_2); 5.87 (s, 1H, pz-H); 5.99 (t, 1H, $^2J_{HH}$ = 16.0 Hz, CH_2); 7.11 (d, 1H, $^3J_{HH}$ = 3.6 Hz, 2-th-H); 7.22 (d, 1H, $^3J_{HH}$ = 4.0 Hz, 3-th-H); 7.50 (s, 4H, BAr_4); 7.68 (s, 8H, BAr_4); 8.07 (s, 1H, CH═N). IR (Diamond ATR, cm^{-1}): 1626 ν(CH═N) imine. Anal. Calcd for $C_{53}H_{44}BrN_4PdSBF_{24}$: C, 44.72; H, 3.09; N, 3.94; S, 2.25. Found: C, 44.43; H, 3.08; N, 3.73; S, 2.55. Positive ion ESI-MS: m/z (%) 502.0 (100%) $[M - Me - NCMe]^+$. Negative ion ESI-MS: m/z (%) 863.0 (100%) $[M]^-$.

2.3. Molecular Structures of 1a and 5a. Single-crystal X-ray diffraction data for compounds **1a** and **5a** were collected on a Bruker APEXII diffractometer with Mo Kα (λ = 0.71073 Å) radiation and a

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detector to crystal distance of 4.00 cm. The initial cell matrix was obtained from three series of scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5° in a 6° range with an exposure time of about 10 s per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The data were collected using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. Data were harvested by collecting 2982 frames at intervals of 0.5° scans in ω and φ with exposure times of 10 s per frame.[15] A successful solution by the direct methods of SHELXS97 provided all non-hydrogen atoms from the *E* map. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms except those on the solvent water molecules were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.[16]

2.4. Copolymerization Procedure for Styrene and Carbon Monoxide. In a stainless steel autoclave (50 mL) containing the catalyst precursor (0.01 mmol) and stirrer was transferred 2.5 mL of styrene and 1 mL of CH_2Cl_2 under an argon atmosphere. In the case of neutral complexes, $Na[BAr_4]$ was added. The system was then charged with CO. The reaction mixture was stirred at 800 rpm at various temperatures, pressures, and time. After the reaction the autoclave was cooled under running tap water, the gas was vented, and the reaction mixture was quenched with MeOH. The crude product (viscous) was purified in CH_2Cl_2/MeOH, and the white polyketone was dried under vacuum overnight.

2.5. Copolymerization Procedure for Ethylene and Carbon Monoxide. In a stainless steel autoclave (50 mL) containing the catalyst precursor (0.01 mmol) and stirrer was transferred 5 mL of CH_2Cl_2 under an argon atmosphere. In the case of neutral complexes, $Na[BAr_4]$ was added. The system was then charged with ethylene and CO. The reaction mixture was stirred at 800 rpm at various temperatures, pressures, and time. After the reaction, the autoclave was cooled under running tap water, the gas was vented, and the dark solid crude product was purified in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The polyketone was in soluble in common organic solvents, and this characteristic was attributed to the high molecular weight of the copolymer.

3. RESULTS AND DISCUSSION

3.1. Syntheses of Ligands and Complexes. Compounds **L1**−**L6**, used as ligands to prepare palladium complexes, were prepared by the condensation of the appropriate aldehyde and alkylpyrazolylamine (Scheme 1) and purified by sublimation to remove unreacted starting materials. Compounds **L1**−**L6** were isolated as oils in yields ranging from 60 to 82%. Reactions of **L1**−**L6** with [PdCl(Me)(cod)] afforded the corresponding complexes **1a**−**6a** in high yields (70−82%) (Scheme 1). Cationic complexes **1b**−**6b** were prepared using $Na[BAr_4]$ to abstract chlorides from complexes **1a**−**6a** (Scheme 1). Ligands **L1** and **L2** behave either as N^N donors in **1a** and **2a** or N^N^N donors in **1b** and **2b**. Ligands **L3**−**L6** behave as bidentate N^N donors in **3a**−**6a** and **3b**−**6b**.

The ligands and their corresponding palladium complexes both exhibited strong IR absorption bands between 1589 and 1692 cm^{-1}, typical of an imine functionality.[17] ^1H NMR spectra of the ligands and complexes also provided useful information in the structural elucidation of all compounds. The ^1H NMR spectra of complexes **3a**,**b** and **5a**,**b** showed two sets of signals for each proton, representing two isomers, but the rest of the complexes showed no isomerization. The isomers were in a ratio of 3:1 (based on integration) representing trans and cis geometries. Complexes with no isomerization are trans. Isomers with the CH_3 group trans to the imine nitrogen are defined as trans in **3a**,**b** and **5a**,**b**, and those with the CH_3 group trans to the pyrazolyl nitrogen are defined as cis in **3a**,**b** and **5a**,**b**. These isomers only exist in solution, since the solid-state structure of **5a** has only the trans isomer in the unit cell. A typical ^1H NMR spectrum that depicts the presence of the trans and cis is given for compound **3a** in Figure S1 (Supporting Information). Here signals for the imine proton[18] were found at 8.32 ppm (trans) and 8.23 ppm (cis). Furthermore, Pd-CH_3 signals were observed at 0.70 ppm (trans) and 0.93 ppm (cis). All the signature peaks for the methyl and thiophene showed similar trans and cis peaks. The peaks for complexes **3b** and **5a**,**b** showed similar peak patterns.

The CH_2CH_2 linker protons in all the palladium complexes were not always well resolved at room temperature. Typical examples are illustrated by complexes **2b** and **6a**. At 25 °C complex **2b** showed four broad peaks between 3.56 and 4.86 ppm, while no signal was observed for **6a**. However, at −50 °C, these protons appeared as two triplets and two doublets in both **2b** and **6a** (Figures 1 and 2, respectively). Our inability to observe linker protons in the ^1H NMR spectra of these complexes could be attributed to the rapid molecular motion of the linker protons at 25 °C, which slows down considerably at −50 °C.

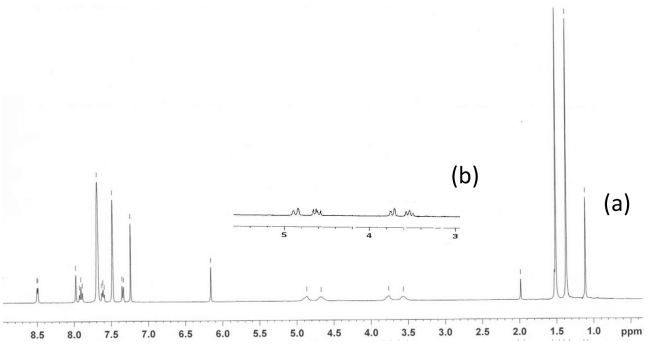

Figure 1. ^1H NMR spectra of **2b** at (a) 25 °C and (b, insert) −50 °C.

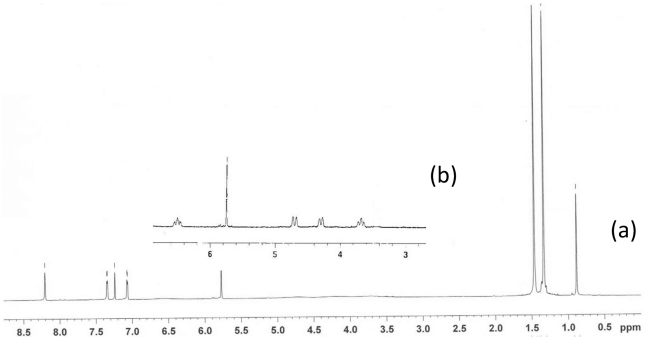

Figure 2. ^1H NMR spectrum of **6a** at (a) 25 °C and (b, insert) −50 °C.

The ^1H NMR spectra of complexes **3b**−**6b** was a singlet between 2.22 and 2.27 ppm, assigned to the methyl of NCMe, indicative of the NCMe stabilizing the palladium center in **3b**−**6b**. In the absence of NCMe, there is instant formation of palladium black, suggesting the sulfur atom in the thiophene is unable to stabilize the palladium center in **3b**−**6b** without a coordinating solvent.

Positive and negative ion mass spectroscopic data were collected for complexes **1b**−**6b**. Molecular ions of the positive species of complexes **1b** and **2b** were obtained at *m*/*z* 349.1 (100%) (Figure S2, Supporting Information) and *m*/*z* 433.0

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(100%), respectively. Complexes **3b**−**6b** did not show the molecular ion but gave various fragments of the molecule, which can be attributed to the individual complexes. The negative ion mass spectroscopic data of complexes **1b**−**6b** showed the counterion molecular ion at m/z 863.0 (100%) (Figure S3, Supporting Information). The mass spectral data confirmed the presence of both the cationic species and the counteranion $[BAr_4]^-$.

3.2. Molecular Structures of 1a and 5a. Single crystals suitable for X-ray analysis of complexes **1a** and **5a** were grown by slow diffusion of hexane into a CH_2Cl_2 solution at −4 °C. Crystallographic data and structural refinement parameters are given in Table S1 (Supporting Information). It must be noted that in the crystal structure of **1a** there is compositional disorder at the C1 site. Namely, 88% of the time this coordination site is occupied by the C1 methyl group and 12% of the time by a Cl atom. Thus, two compounds with different compositions cocrystallized in the crystal selected for the analysis. Hereafter we will concentrate on the discussion of the major component of complexes **1a** and **5a**.

Molecular structures of **1a** and **5a** are shown in Figures 3 and 4, respectively, while selected bond lengths and angles of these complexes are given in the figure captions. The Pd coordination geometry in both complexes is distorted square planar. The observed bond angles for N(1)−Pd(1)−C(1) are 96.68(19)° in **1a**, and 91.80(2)° in **5a**, showing deviations from planarity and ideal geometry. The Pd−CH_3 bond length is 2.018(5) Å in **1a**

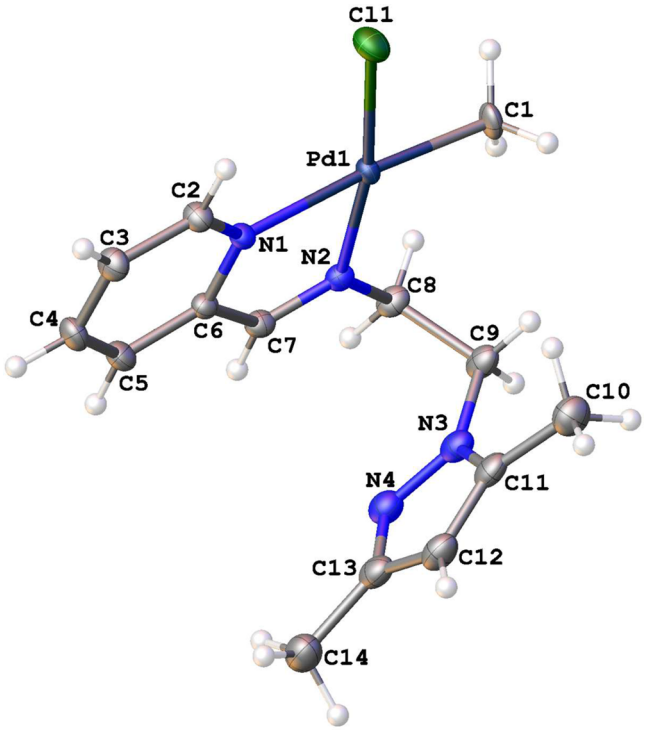

Figure 3. Molecular structure of **1a**, drawn with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd(1)−N(1), 2.1252(15); Pd(1)−N(2), 2.0573(14); Pd(1)−Cl(1), 2.267(8); Pd(1)−C(1), 2.018(5); N(2)−C(8), 1.462(2); N(1)−C(6), 1.354(2); C(8)−C(9), 1.523(2); C(1)−Pd(1)−N(2), 96.68(19); C(1)−Pd(1)−N(1), 174.9(2); N(2)−Pd(1)−N(1), 79.31(5); C(1)−Pd(1)−Cl(1), 89.8(2); N(2)−Pd(1)−Cl(1), 169.86(4); N(1)−Pd(1)−Cl(1), 94.61(4); C(2)−N(1)−C(6), 118.63(14); N(1)−Pd(1)−Cl(1), 94.61(4); N(1)−C(6)−C(7), 114.71(14).

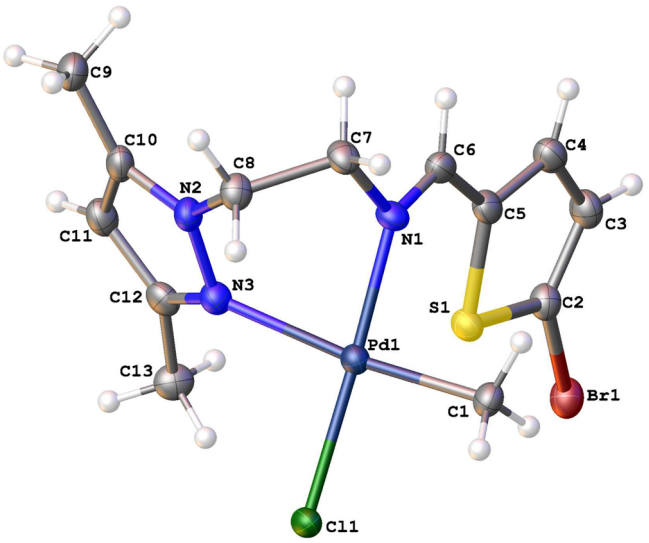

Figure 4. Molecular structure of **5a**, drawn with 50% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Pd(1)−N(1), 2.020(5); Pd(1)−N(3), 2.173(6); Pd(1)−Cl(1), 2.3217(13); Pd(1)−C(1), 2.034(6); N(2)-(N(3), 1.362(7); N(1)−Pd(1)−C(1), 91.8(2); N(1)−Pd−N(3), 81.48(19); N(1)−Pd−Cl(1), 177.65(14); C(1)−Pd(1)−N(3), 172.5(2); N(3)−Pd(1)−Cl(1), 96.96(13); C(1)−Pd−Cl(1), 89.60(17).

and 2.034(6) Å in **5a**, and this difference is probably statistically significant. Interestingly, in both structures the Pd−N distance to the imine N atom situated in the middle of the ligand is substantially shorter (∼0.07 and ∼0.12 Å in **1a** and **5a**) than that to the N ligand at the pyrazole or pyridine ring. The observed Pd−CH_3 bond lengths in **1a** and **5a** are in good agreement with similar bond lengths (2.055(38) Å) averaged for 351 relevant palladium complexes reported to the Cambridge Structural Database (CSD).[19] The Pd−Cl bond length was recorded as 2.267(8) Å in **1a** and 2.3217(13) Å in **5a**, which are statistically different but are in the range (2.242−2.516 Å) reported for 1776 relevant palladium complexes in the Cambridge Structural Database (CSD).[19] The different palladacycle sizes in **1a** and **5a** expectedly result in different N−Pd−N angles: 79.31(5)° for the five-membered cycle in **1a** and a much less strained 81.48(19)° for the six-membered cycle in **5a**.

3.3. Copolymerization Reaction of Olefins/CO Catalyzed by Complexes 2b and 3b. Complexes **1a**−**6a** were screened as catalyst precursors for the reactions of ethylene/CO and styrene/CO in a 1:1 mixture of CH_2Cl_2 and NCMe when equimolar amounts of $Na[BAr_4]$ were added to each precursor. Invariably, these attempts resulted in the production of palladium black. Subsequently the cationic species **1b**−**6b** were prepared in stoichiometric reactions as precursors to the olefin/CO copolymerization reactions above. With the exception of **2b** and **3b**, (Scheme 2) all of the other cationic species had very low activities, invariably decomposing to palladium black. Even for **2b** and **3b** there were significant amounts of palladium black formation, hence their moderate activities.

Both types of polyketones were characterized by a combination of NMR, IR, GPC, and thermal analyses. A typical $^{13}C\{^1H\}$ NMR spectrum (Figure S4, Supporting Information) of the styrene/CO copolymer showed a methylene carbon at 43 ppm, a tertiary carbon at 53 ppm, phenyl carbons between 126 and 128 ppm, ipso carbon peaks

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Scheme 2. Copolymerization Reaction of Styrene/CO and Ethylene/CO

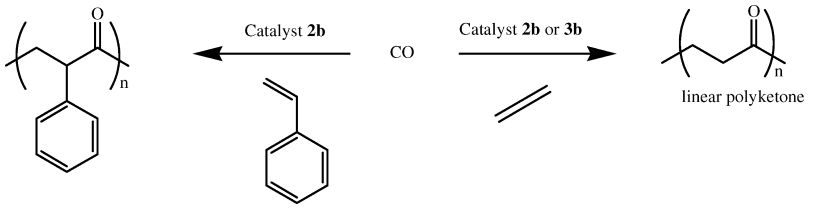

Table 1. Styrene and Carbon Monoxide Copolymerization Catalyzed by 2b[a]

entry	temp, °C	time, h	pressure, MPa	yield,[b] mg	activity, g mol^{-1} h^{-1}	M_w[c]	M_n[c]	PDI[c]	TON	selectivity[d] ll:(ul:lu):uu
1	25	24	1	100	420	23200	21900	1.06	0.46	0:9:18:73
2	40	24	1	190	790	28400	16 100	1.76	1.17	0:11:11:78
3	60	24	1	110	460	8400	5900	1.42	1.84	0:11:11:78
4	40	3	1	120	4000	10100	9200	1.10	1.30	0:11:11:78
5	40	12	1	140	1170	15400	9100	1.69	1.54	0:11:11:78
6	40	48	1	220	460	35300	24000	1.47	0.92	0:11:11:78
7	40	3	3	50	1670	4100	3500	1.15	1.40	0:11:11:78
8	40	24	5	60	250	8 700	6300	1.39	0.95	0:11:11:78

[a]Conditions: catalyst precursor, 0.01 mmol; styrene:Pd = 2100:1; CH_2Cl_2 volume, 1.0 mL. [b]Yield after purification. [c]Determined by GPC. [d]Determined by $^{13}C\{^1H\}$ NMR spectroscopy.

Table 2. Ethylene and Carbon Monoxide Copolymerization Catalyzed by 2b and 3b[a]

entry	cat.	temp, °C	time, h	ethylene pressure, MPa	CO pressure, MPa	yield,[b] mg	activity, g mol^{-1} h^{-1}
1	**2b**	25	24	2	1	110	460
2	**2b**	40	24	2	1	210	880
3	**3b**	25	24	2	1	95	395
4	**3b**	40	24	2	1	184	767
5	**2b**	40	3	2	1	60	2000
6	**2b**	40	3	3	1	100	3330
7	**3b**	40	3	2	1	51	1700
8	**3b**	40	3	3	1	83	2767
9	**2b**	40	3	4	1	140	4670
10	**2b**	40	12	4	1	165	1380
11	**2b**	40	18	4	1	190	1060
12	**3b**	40	3	4	1	110	3667
13	**3b**	40	12	4	1	153	1275
14	**3b**	40	18	4	1	170	944
15	**2b**	40	3	4	2	40	1330
16	**2b**	40	3	3	3	40	1330
17	**3b**	40	3	4	2	40	1330
18	**3b**	40	3	3	3	40	1 330
19	**2b**	60	3	4	1	110	3670
20	**3b**	60	3	4	1	100	3333

[a]Conditions: catalyst precursor, 0.01 mmol; CH_2Cl_2 volume, 5.0 mL. [b]Yield after purification.

at 136, 137, and 138 ppm indicative of three stereoisomers, and a carbonyl carbon peak at 206.4 ppm. The stereoslectivity of C_1-symmetry ligands such as those reported here are hardly predictable in comparison to enantiopure C_2 or C_{2v} symmetry ligands, which as a rule of thumb give optically active isotactic and syndiotactic polyketones, respectively.[20] The stereochemistry for the polyketone produced with our catalysts showed that three ipso carbon peaks, which were assigned as uu (unlike−unlike), ul (unlike−like), and lu (like-unlike). The uu isomer was dominant (78%); hence, the stereochemistry of the copolymer is syndiotactic.[21,22]

The $^{13}C\{^1H\}$ NMR and ^1H NMR (Figure S5, Supporting Information) spectra showed that the polyketones formed are perfectly alternating.

IR spectra of the styrene/CO copolymers showed a strong absorption band in the range 1695.3−1708.8 cm^{-1}, assigned to the carbonyl functionality, a methylene band in the range 2906.5−2910.4 cm^{-1}, and monosubstituted benzene bands at 696 and 748 cm^{-1} (Figure S6, Supporting Information). These are indicative of CO and styrene as pendant groups on the polyketone backbone.

Differential scanning calorimetry (DSC) of styrene/CO copolymers gave T_g values in the range 112.2−116.5 °C. However, no T_m values were observed. This suggests that the copolymer could be either amorphous or semicrystalline. The polyketone decomposed above 360.6 °C, as shown by TGA experiments (Figure S7, Supporting Information).

The reaction parameters of catalyst **2b** for styrene/CO copolymerization are shown in Table 1. Temperature variation

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from 25 to 60 °C showed activity and molecular increase from 25 to 40 °C but decreased at 60 °C (Table 1, entries 1 and 2) with no significant change in stereochemistry. This suggests that at 60 °C there is some deactivation of catalyst and the solubility of CO in the liquid phase is low. Similar observations have been reported.[23] Furthermore, an increase in temperature above 60 °C resulted in the formation of polystyrene, which was attributed to free radical polymerization of styrene at high temperatures.[24]

Time variation from 3 to 48 h showed a decrease in activity and increase in molecular weight, suggesting catalyst deactivation with time (Table 1, entries 4−6). An increase in CO pressure resulted in a decrease in activity and molecular weight (Table 1, entries 7 and 8). This is because at high CO pressure CO coordinates strongly to the palladium center, therefore retarding the coordination−insertion of olefin. Catalyst **2b** was observed to have optimum reaction conditions at 1 MPa of CO, 40 °C, and 3 h which gives an activity of 4000 g mol h^{-1}.

Complexes **2b** and **3b** catalyzing the ethylene/CO copolymerization reaction produced alternating copolymers, which were insoluble in common organic solvents. $^{13}C\{^1H\}$ (Figure S8, Supporting Information) and ^1H NMR (Figure S9, Supporting Information) spectroscopic data of the copolymers were obtained in both HFIP and $CDCl_3$. The $^{13}C\{^1H\}$ NMR spectra showed methylene carbons and carbonyl carbons in a ratio of 2:1 at 35.4 and 212.9 ppm, respectively. This and the ^1H NMR spectrum, which showed only a singlet at 2.78 ppm, suggest that the ethylene/CO copolymer was a perfectly alternating polyketone. IR spectrum (Figure S10, Supporting Information) also showed a strong carbonyl peak at 1693 cm^{-1} and a methylene peak at 2912 cm^{-1}, indicating the presence of CO and saturated ethylene in the polyketone backbone.

DSC experiments performed on the copolymers gave T_g values in the range 41.9−45.2 °C and T_m values in the range 263−268 °C. The observation of a T_m value showed that the copolymer was crystalline. The polyketones decomposed above 325.5 °C.

Catalysis data (Table 2) showed that the activities of **2b** and **3b** increased with temperature from 25 to 40 °C (Table 2, entries 1−4) but decreased at 60 °C (Table 2, entries 19 and 20) with no change in the nature of the polyketone. However, increasing the temperature above 60 °C gave no activity. This suggests that both catalysts deactivate or decompose at higher temperatures.

A time study from 3 to 18 h showed activities decreasing as the reactions were run for longer times (Table 2, entries 9−14), suggesting catalyst deactivation with time. Increasing the CO pressure decreased the activities of both catalysts (Table 2, entries 15−18). Furthermore, an increase in ethylene pressure resulted in an increase in activity for both catalysts (Table 2, entries 5−8), which agrees with previous reports.[2,3] Optimum conditions for both **2b** and **3b** of the catalytic reaction are 40 °C, 1 MPa of CO, 3 h, and 4 MPa of ethylene, giving activities of 4670 and 3667 g mol^{-1} h^{-1}, respectively (Table 2, entries 9 and 12).

Complex **2b** performed better as an ethylene/CO catalyst in comparison to styrene/CO copolymerization. That is, under optimum conditions, the activity of **2b** as catalyst for ethylene/CO copolymerization was 4670 g mol^{-1} h^{-1} (Table 2, entry 9) while styrene/CO gave 4000 g mol^{-1} h^{-1} (Table 1, entry 4). This could be due to the steric bulk of styrene, which slows the insertion process. In both type of copolymerizations, catalyst **2b** decomposes at temperatures above 60 °C and also gradually deactivates with time.

4. CONCLUSION

Pyrazolylimine hemilabile ligands and their palladium complexes were prepared. These ligands show that the pyrazolyl nitrogen atom is a weak donor in comparison to the pyridine nitrogen atom but a stronger donor than thiophene sulfur. In situ generation of the active catalysts with $Na[BAr_4]$ under copolymerization conditions resulted in very low activities and the formation of palladium black. However, presynthesized cationic species showed moderate olefin/CO copolymerization activities. Comparing the activities of **2b** and **3b** to those of other nitrogen-based palladium complexes such as 2,2′-bipyrindine and 1,10-phenanthroline reported in the literature revealed that **2b** and **3b** have low activities.

■ ASSOCIATED CONTENT

Supporting Information

Figures, CIF files, and a table giving additional characterization data and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for structural analysis have also been deposited with the Cambridge Crystallographic Data Centre: CCDC 885488 and 885489. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44−1223−336063; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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