Ambidentate Character of the 6-Aminofulvene-2-aldiminate Ligand Containing Both Diimine and Cyclopentadienyl Donors

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The 6-aminofulvene-2-aldiminate (AFA) ligand contains both cyclopentadienyl and diimine donors. The ligand preferentially coordinates to transition metals via the nitrogen atoms; however once these are occupied, the cyclopentadienyl ring may be coordinated to a Cp*Ru$^+$ unit, providing bi- and trimetallic species. In the tetrahedral [Zn(Ph$_2$AFA)$_2$] (**2**) the metal is located approximately in the planes of the two ligands; however in the square-planar [Pd(Ph$_2$AFA)$_2$] (**1**) there is a severe distortion of the coordination and the metal is located almost 1.3 Å out of the planes of the two ligands. This situation arises to avoid the steric interaction of the ligand phenyl substituents. Treatment of **2** with [Cp*Ru(NCMe)$_3$][BF$_4$] gives [Cp*Ru(η^5-Ph$_2$AFA)] (**3**), providing the first example of the cyclopentadienyl coordination of an AFA ligand in which the nitrogen donors are vacant, and it is thought to form as a result of the fragmentation of an intermediate mixed Zn/Ru species. The X-ray structure of **3** provides some evidence for an interaction between the Ru center and one of the exocyclic carbon atoms, thus suggesting a fulvene form of the ligand in this complex. Similar treatment of **1** with [Cp*Ru(NCMe)$_3$][BF$_4$] provides a trimetallic PdRu$_2$ species (**4**) in which both of the cyclopentadienyl rings in the complex **2** are coordinated to Ru. The complex [(Ph$_2$AFA)Pd(Me)PPh$_3$] (**5**) is formed on treatment of [(COD)PdMe(Cl)] with NaPh$_2$AFA in the presence of PPh$_3$, and preliminary investigations have shown that its activation with [Ni(COD)$_2$] as a phosphine scavenger provides species active toward ethylene oligomerization and polymerization.

Introduction

The 6-aminofulvene-2-aldimine (AFAH) system was first prepared in 1963,[1] but its chemistry, in particular its properties as a ligand, has received very little attention. Our earlier studies of this system provided two novel magnesium species, one of which showed the 6-aminofulvene-2-aldiminate (AFA) system acting as an ambidentate ligand, coordinated to metal centers through both the nitrogen and the C$_5$-ring donors.[2] Two resonance forms of the ligand may be drawn (Figure 1), and the ability of the cyclopentadienyl portion of the ligand to symmetrically coordinate to a metal in a pentahapto mode indicates that form **B** makes a significant contribution. This feature of the ligand provides the potential for the formation of charge-neutral but zwitterionic analogues of cationic complexes containing conventional neutral diimine ligands when the cyclopentadienyl portion of the ligand remains uncoordinated. This could have particular significance in strongly electrophilic, positively charged catalysts for which the presence of a counterion often presents problems by coordinating to the metal center. One such case is the class of square-planar group 10 transition metal alkene polymerization catalysts formed by Lewis acid activation of [(1,2-diimine)MMe$_2$] (M = Ni, Pd) complexes.[3] Replacement of the 1,2-diimine ligand in these systems with an AFA ligand would provide a neutral complex that retains significant positive charge at the metal by virtue of the contribution from resonance form **B** to the ligand electronic structure (Figure 2) and would furthermore provide catalysts that would not require Lewis acid activation. With this in mind we have initiated a study of the late transition metal coordination chemistry of the AFA ligand system. We report here the unusual coordination geometry adopted by the AFA ligand in square-planar Pd(II) complexes, and the ability of the ligand to coordinate to Ru(II) via the cyclopentadienyl ring, in complexes in which the diimine portion of the ligand is either metal coordinated or vacant. Preliminary results from a study of ethene oligomerization/polymerization by [(Ph$_2$AFA)Pd(Me)PPh$_3$] (**5**) activated by the phosphine scavenger [Ni(COD)$_2$] are also reported.

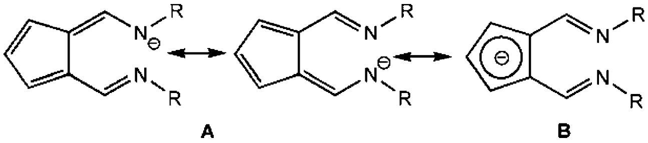

Figure 1. Resonance forms for the 6-aminofulvene-2-aldiminate ligand.

Experimental Section

All reactions and manipulations of moisture- and air-sensitive compounds were carried out in an atmosphere of dry nitrogen using Schlenk techniques or in a conventional nitrogen-filled glovebox (Saffron Scientific), fitted with oxygen and water scavenging columns. All the solvents were purified and dried by means of distillation over an appropriate drying agent prior to use. Toluene, THF, diethyl ether, hexane, and benzene were all distilled from Na/benzophenone under a nitrogen atmosphere. NMR solvents were

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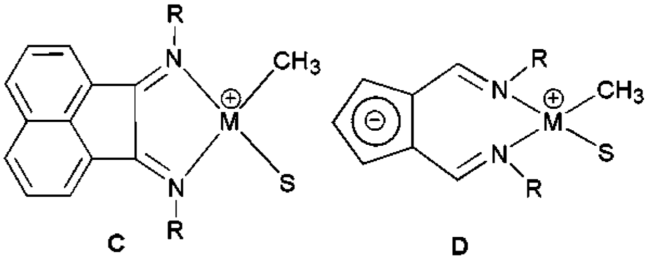

Figure 2. 1,2-Diimine group-10 metal alkene polymerization catalysts (**C**, M = Ni, Pd; S = solvent) and the possible neutral zwitterionic analogue containing an AFA ligand (**D**).

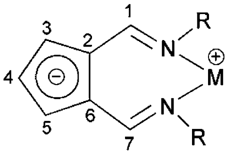

Figure 3. C/H atom numbering scheme used in the assignment of the NMR spectra of the AFA complexes.

degassed using freeze−thaw cycles and stored over 4 Å molecular sieves. The ligand Ph_2AFAH,[1] [(COD)PdMe(Cl)],[4] and the salt $[Cp^*Ru(CH_3CN)_3][BF_4]$[5] were prepared according to the literature procedures, while $[Ni(COD)_2]$ was purchased from Aldrich and used as received. Polymer-grade ethylene was purchased from BOC gases and used as received. All solvents and other reagents were purchased from Sigma-Aldrich, Fischer, or Acros and used as received unless otherwise stated. Column chromatography was performed on silica gel (Merck 60, 7−120 mesh). NMR spectra were recorded on Bruker AC 250 and 360 MHz spectrometers operating at room temperature, except for the ^{13}C spectrum of the polyethylene, which was recorded at 120 °C. ^1H and ^{13}C chemical shifts are reported in ppm relative to $Si(CH_3)_4$ ($\delta = 0$) and were referred internally with respect to the protio solvent impurity or ^{13}C resonances, respectively. The C/H atom numbering scheme used in the assignment of the NMR spectra of the AFA complexes is shown in Figure 3. Polyethylene GPC analysis was undertaken by RAPRA Technology (Shrewsbury, UK) using a 30 cm × 10 μm PLgel guard plus 2× mixed bed-B column at 160 °C in 1,2,4-trichlorobenzene solution. Refractive index and Viscotek differential pressure detectors were employed and calibrated with polystyrene.

$[(Ph_2AFA)_2Pd]$ (1). To a solution of Ph_2AFAH (0.30 g, 1.10 mmol) in 25 mL of toluene was added 0.7 mL of CH_3Li (1.6 M in THF) and the mixture stirred for 1 h. A solution of $(PhCN)_2PdCl_2$ (0.210 g, 0.55 mmol) in toluene (50 mL) was stirred at 50 °C for 30 min and then added via cannula. The mixture was stirred at room temperature for 2 h and then filtered through a pad of Celite. The volume was reduced in vacuo to 10 mL and the solution stored at −5 °C for 1 day. The dark purple crystalline solid formed was separated by filtration, washed twice with 2 × 10 mL portions of hexanes to remove small amounts of free ligand, and dried under vacuum. Yield: 39.5% (0.217 mmol, 0.141 g). Crystals suitable for X-ray analysis were obtained from THF solutions upon slow evaporation of the solvent. ^1H NMR (360 MHz, CD_2Cl_2): δ 7.44 (s, 2H, *H*1/*H*7), 7.45−7.42 (d, 4H, ortho-C_6H_5), 7.29−7.25 (t, 4H, meta-C_6H_5), 7.20−7.15 (t, 2H, para-C_6H_5), 6.70 (d, 2H, *H*3/*H*5, $^3J = 3.63$ Hz), 6.38 (t, 1H, *H*4, $^3J = 3.63$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90.6 MHz, 20 °C): δ 160.44 (*C*=N), 149.03 (N-C_6H_5), 135.16 (C_6H_5), 128.53 (C_6H_5), 125.35 (*C*3/*C*5), 122.87 (C_6H_5), 120.56 (*C*2/*C*6), 117.39 (*C*4). Although attempts at elemental analysis were made, they were not satisfactory. However, the ^{13}C NMR spectrum is consistent with the structure determined by X-ray crystallography and indicates the absence of carbon-containing impurities.

$[(Ph_2AFA)_2Zn]$ (2). To a solution of Ph_2AFAH (0.40 g, 1.47 mmol) in 30 mL of THF was added NaH, and immediately gas evolution was observed. The mixture was stirred for 1 h, and a solution of anhydrous $ZnCl_2$ (0.098 g, 0.735 mmol) in THF (30 mL) was added via cannula. After stirring for 3 h, the solution was filtered through Celite and the solvent was removed in vacuo. The solid was extracted with 30 mL of CH_2Cl_2 and the solvent removed to yield a yellow crystalline solid. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solvent from hexane solutions of the product. ^1H NMR ($CDCl_3$, 360 MHz, 20 °C): δ 8.05 (s, 4H, *H*1/*H*7), 7.01 (d, 4H, *H*3/*H*5, $^3J = 3.65$ Hz), 7.00−6.97 (m, 12H, C_6H_5), 6.84−6.80 (m, 8H, C_6H_5), 6.39 (t, 2H, *H*4, $^3J = 3.65$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 90.6 MHz, 20 °C): δ 162.94 (*C*=N), 150.69 (N-C_6H_5), 139.82 (C_6H_5), 128.87 (C_6H_5), 125.05 (*C*3/*C*5), 122.19 (C_6H_5), 118.67 (*C*2/*C*6), 117.99 (*C*4). Anal. Calcd for $C_{38}H_{30}N_4Zn$: C, 75.06; H, 4.97; N, 9.21. Found: C, 75.33; H, 4.58; N, 8.86.

$[Cp^*Ru(Ph_2AFA)]$ (3). $[Cp^*Ru(CH_3CN)_3][BF_4]$ (0.250 g, 0.559 mmol) and $(Ph_2AFA)_2Zn$ (0.339, 0.559 mmol) were dissolved in CH_2Cl_2 (30 mL), and the mixture was stirred for 1 h. After cannula filtration, 30 mL of diethyl ether was carefully layered onto the solution. Upon standing for 1 day, crystals suitable for X-ray analysis had formed, which were isolated and dried under vacuum. The ^1H NMR spectrum of **3** showed it to be protonated (**3**H^+). ^1H NMR (CD_2Cl_2, 360 MHz, 20 °C): δ 16.51 (bt, N-H^+-N, $^3J = 7$ Hz), 8.95 (d, 2H, *H*1/*H*7, $^3J = 7$ Hz), 7.52−7.39 (m, 10H, C_6H_5), 5.66 (d, 2H, *H*3/*H*5, $^3J = 2.99$ Hz), 4.20 (t, 1H, *H*4, $^3J = 2.99$ Hz), 1.85 (s, 15H, CpCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90.6 MHz, 20 °C): δ 161.37 (*C*=N), 142.66 (N-C_6H_5), 130.59 (*m*-C_6H_5), 128.45 (*p*-C_6H_5), 119.91 (*o*-C_6H_5), 92.57 (C_5Me_5), 85.47 (*C*3/*C*5), 84.91 (*C*2/*C*6), 79.47 (*C*4), 11.50 (C_5Me_5). MS (FAB, *m/z*): 309 (M^+). Treatment of a THF solution of **3**H^+ with NaH resulted in the removal of the N−H···N proton, and the NMR spectra of **3** in carefully dried CD_2Cl_2 could be obtained. ^1H−NMR (CD_2Cl_2, 360 MHz, 25 °C): δ 8.59 (s, 2H, *H*1/*H*7), 7.37−7.12 (m, 10H, C_6H_5), 5.05 (d, 2H, *H*3/*H*5, $^3J = 2.83$ Hz), 4.67 (t, 1H, *H*4, $^3J = 2.83$ Hz), 1.87 (s, 15H, CpCH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 90.6 MHz, 20 °C): δ 159.36 (*C*=N), 153.09 (N-C_6H_5), 129.07 (*m*-C_6H_5), 124.99 (*p*-C_6H_5), 120.67 (*o*-C_6H_5), 88.09 (C_5Me_5), 83.83 (*C*3/*C*5), 77.20 (*C*2/*C*6), 76.02 (*C*4), 11.83 (C_5Me_5). Although attempts at elemental analysis were made, they were not satisfactory. However, the ^{13}C NMR spectrum is consistent with the structure determined by X-ray crystallography and indicates the absence of carbon-containing impurities.

$[(Cp^*Ru)_2Pd(Ph_2AFA)_2][BF_4]_2$ (4). $[Cp^*Ru(CH_3CN)_3][BF_4]$ (0.250 g, 0.559 mmol) and $(Ph_2AFA)_2Pd$ (0.181 g, 0.280 mmol) were stirred in CH_2Cl_2 (40 mL) for 1 h, and the solution was filtered via cannula. After storage at −5 °C for 2 days, crystals of the desired compound had formed as orange blocks. They were isolated via filtration and dried in vacuo. Yield: 46.0% (0.167 g, 0.129 mmol). Crystals suitable for X-ray analysis were obtained from $CHCl_3$ solution via slow evaporation of the solvent. ^1H NMR (CD_3OD, 360 MHz, 25 °C): δ 7.91 (s, 4H, *H*1/*H*7), 7.70−7.67 (m, 8H, m-C_6H_5), 7.56−7.53 (m, 12H, C_6H_5), 5.66 (t, 2H, *H*4, $^3J = 2.80$ Hz), 5.40 (d, 4H, *H*3/*H*5, $^3J = 2.80$ Hz), 1.58 (s, 30H, CpCH_3). $^{13}C\{^1H\}$ NMR (CD_3OD, 90.6 MHz, 25 °C): δ 168.47 (*C*=N), 147.91 (N-C_6H_5), 131.02 (C_6H_5), 130.32 (C_6H_5), 123.81 (C_6H_5), 96.01 (*C*4), 88.11 (*C*2-*C*6), 86.18 (C_5Me_5), 77.58 (*C*3-*C*5), 11.57 (C_5Me_5). Anal. Calcd for $C_{58}H_{60}N_4B_2F_8Ru_2Pd$: C, 53.78; H, 4.67; N, 4.33. Found: C, 53.39; H, 4.43; N, 4.13.

$[(Ph_2AFA)Pd(CH_3)PPh_3]$ (5). To a solution of Ph_2AFAH (0.30 g, 1.10 mmol) in toluene (25 mL) was added 0.7 mL of CH_3Li (1.6 M in THF) and the mixture stirred for 1 h. To a solution of $[(COD)Pd(CH_3)(Cl)]$ (0.290 g, 1.10 mmol) in toluene (10 mL) was added PPh_3 (0.288 g, 1.10 mmol), and after stirring for 5 min, the

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Table 1. Crystal Data for Compounds 1, 2, 3, 4, and 5

	1	2	3	4	5
cryst description	red block	yellow block	red block	orange block	dark red block
empirical formula	$C_{42}H_{38}N_4OPd$	$C_{38}H_{30}N_4Zn$	$C_{31}H_{34}Cl_2N_2Ru$	$C_{60}H_{62}B_2Cl_6F_8N_4PdRu_2$	$C_{38}H_{33}N_2PPd$
M_w	721.16	608.03	606.57	767.02	655.03
T (K)	150(2)	150(2)	220(2)	150 (2)	150 (2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$I2/a$	$P2_1/c$	$P2_1$	$P2_1/c$	$P2_1/n$
a (Å)	16.7396(7)	10.0428(3)	11.1538(4)	11.0330(2)	9.0131(3)
b (Å)	19.2569(8)	18.9776(7)	11.6438(4)	15.3253(3)	19.7765(8)
c (Å)	10.3606(5)	15.4767(6)	12.7666(4)	19.1861(4)	17.4028(8)
α (deg)	90	90	90	90	90
β (deg)	90.412(2)	93.126(2)	114.164(2)	104.6070(10)	99.393(3)
γ (deg)	90	90	90	90	90
V (Å^3)	3339.7(3)	2945.29(18)	1512.75(9)	3139.21(11)	3060.4(2)
Z	4	4	2	2	4
μ(Mo Kα) (mm^{-1})	0.596	0.868	0.716	1.079	0.688
no. of indep reflns	4725 [R(int) = 0.0332]	6457 [R(int) = 0.0520]	5391 [R(int) = 0.0311]	8342 [R(int) = 0.039]	9135 [R(int) = 0.0333]
no. of data with $\|F\| > 4\sigma(\|F\|)$	3997	4600	5090	7050	3534
absorp corr	multiscan ($T_{min} = 0.769$, $T_{max} = 0.910$)	multiscan ($T_{min} = 0.627$, $T_{max} = 0.840$)	multiscan ($T_{min} = 0.698$, $T_{max} = 0.880$)	semiempirical from equivalents ($T_{min} = 0.66$, $T_{max} = 0.87$)	multiscan ($T_{min} = 0.682$, $T_{max} = 0.810$)
R	0.0401	0.0437	0.0337	0.0489	0.0313
R_w	0.1002	0.1031	0.0900	0.1188	0.0826

resulting suspension was added by means of a cannula into the solution of the deprotonated ligand. The mixture was stirred for 3 h and then filtered through Celite. Upon slow evaporation of the solvent [$(Ph_2AFA)Pd(PPh_3)(CH_3)$] was obtained as red crystals suitable for X-ray analysis (0.346 g, 48%). ^{1}H NMR ($CDCl_3$, 360 MHz, 20 °C): δ 8.53 (d, 1H, *H*1, $^3J = 8.20$ Hz), 8.00 (s, 1H, *H*7), 7.52 (d, 2H, C_6H_5), 7.31−7.39 (m, 9H, P-C_6H_5), 7.25−7.20 (m, 6H, P-C_6H_5), 7.12 (t, 1H, C_6H_5), 7.01 (t, 1H, C_6H_5), 6.93 (dd, 1H, *H*3, $^3J = 3.57$ Hz), 6.77 (dd, 1H, *H*5, $^3J = 3.57$ Hz), 6.45 (t, 1H, *H*4, $^3J = 3.57$ Hz), −0.021 (d, 3H, CH_3, $J = 3.57$ Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 90.6 MHz, 25 °C): δ 160.71 (C1), 158.43 (C7), 150.80 (C8), 150.10 (C12), 134.16 (C17, $^2J_{C-P} = 11.7$ Hz), 131.79 (*C*15), 131.39 (*C*11), 130.89 (*C*16, $^1J_{C-P} = 48.9$ Hz), 130.09 (*C*19), 128.77 (*C*14), 128.30 (*C*10), 127.94 (*C*18, $^3J_{C-P} = 10.3$ Hz), 124.39 (*C*3), 123.84 (*C*5), 122.96 (*C*13), 121.16 (*C*9), 119.28 (*C*2), 119.13 (*C*6), 118.06 (*C*4), 3.55 (CH_3, $^2J_{C-P} = 8.5$ Hz). Anal. Calcd for $C_{38}H_{33}N_2PPd$: C, 69.67; H, 5.08; N, 4.28. Found: C, 69.36; H, 4.97; N, 4.15.

General Procedure for Reactivity Studies with Ethylene. A Büchi glass autoclave (100 mL) was heated at 80 °C under vacuum for 3 h and then cooled to room temperature under an ethylene atmosphere. The autoclave was charged with 20 mL of toluene and then sealed. The pressure of ethylene was set to the desired value, and the desired temperature was established by means of an oil bath. After releasing the pressure, a solution of **5** (75 μmol in 5 mL of toluene) and [$Ni(COD)_2$] (150 μmol in 5 mL of toluene) were added in sequence via cannula. The reactor was sealed and pressurized with ethylene to the desired reaction pressure. The reaction mixture was stirred under constant pressure for 6 h, after which time the pressure was released and the catalyst quenched with acidified methanol. An aliquot of the mother liquor was analyzed by EI-MS to detect formation of oligomers, whereas the solid polymer produced was collected by filtration and dried overnight under vacuum.

Crystallography. Data were collected at 150 K (220 K for 3) on a Bruker Smart APEX diffractometer equipped with an Oxford Cryosystems low-temperature device. The structures were solved with Patterson methods (DIRDIF)[6] and refined using SHELXL or Crystals.[7,8] The crystal data for compounds **1**, **2**, **3**, **4**, and **5** are provided in Table 1. In **1** the complex sits with the Pd atom on an inversion center. The structure contains a molecule of THF disordered about a 2-fold axis. The atom labeled C1S is common to both disorder components and is full-occupancy. The other atoms (C2S, C3S, and C4S) are half-weight. Crystals of **3** appeared to shatter at 150 K, and data were therefore collected at 220 K. Disordered solvent regions were treated with the Squeeze procedure.[9] Compound **4** crystallizes with two molecules of chloroform in the unit cell.

Results and Discussion

Treatment of *N*,*N*′-diphenyl-6-aminofulvene-2-aldimine (Ph_2-AFAH) with butyl lithium in toluene followed by reaction with [$(PhCN)_2PdCl_2$] provides [Pd(κ^2-$Ph_2AFA)_2$] (**1**). This is the only product that may be isolated for either 1:1 or 2:1 (ligand:Pd) reaction stoichiometries. The crystal structure (Figure 4) shows that the complex is centrosymmetric and that the two ligands are therefore equivalent. The coordination of the ligand is highly unusual, with the mean plane of the ligand atoms being tilted toward an axial position relative to the square-planar environment of the metal. Similar, although less marked, deviations from coplanarity of the metal and ligand atoms have been observed in complexes of the related AFA ligand $[\{HN{=}C(Ph)\}_2C_5H_3]^-$.[10] The acute angle between the PdN_4 plane and the mean plane defined by the two N═C imine bonds (θ) in **1** is 53.6°, and the displacement of the metal from this plane (ω) is 1.27 Å (Figure 5). This unusual coordination geometry is not accompanied by any significant distortion of the N−Pd−N chelate angle [92.89(8)°]. The C−C (C3−C2 and C7−C8) bond lengths within the chelate ring are crystallographically indistinguishable, as are the C−N (C2−N1 and C8−N9) bond lengths, thus supporting the view of the ligand as a cyclopentadienyl−diimine (**B**, Figure 1). The C_5 ring of the ligand is planar; however, the imine CH carbon atoms lie 0.105 Å (C2) and 0.264 Å (C8) above this plane, while the nitrogen atoms are 0.165 (N1) and 0.078 (N9)

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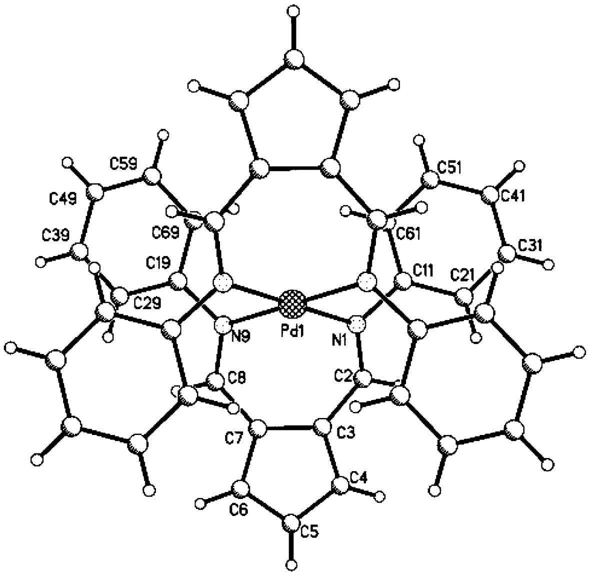

Figure 4. Molecular structure of [Pd(κ^2-Ph$_2$AFA)$_2$] (**1**). Selected bond lengths (Å) and angles (deg): Pd−N1 2.028(2), Pd−N9 2.0369(19), N1−C2 1.308(3), C2−C3 1.412(3), C3−C7 1.446(3), C7−C8 1.413(3), C8−N9 1.309(3), N1−Pd−N9 92.89(8), Pd−N1−C2 121.55(17), N1−C2−C3 127.6(2), C2−C3−C7 131.4(2), C3−C7−C8 130.7(2), C7−C8−N9 127.2(5), C8−N9−Pd 118.86(16).

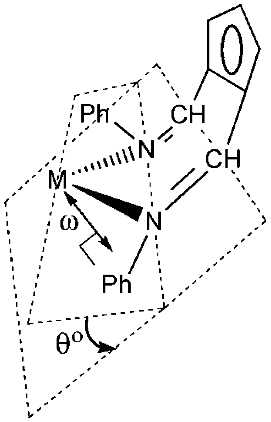

Figure 5. Parametrization of the Ph$_2$AFA ligand coordination geometry. $\theta°$ = the acute angle between the plane defined by the metal and the two ligand nitrogen atoms and the mean plane defined by the two ligand C═N bonds; ω = the displacement of the metal from this plane.

Å below and above it, respectively. The Pd−N−C angles are close to 120°; the remaining angles in the chelate ring are however considerably greater than 120°, but do not differ by more than 1° from the corresponding angles in the free ligand (Ph$_2$AFAH) in which all the non-phenyl atoms are coplanar and there is a strong N−H−N intramolecular hydrogen bond.[11] Furthermore, the intraligand N1−N9 distance of 2.946 Å in **1** is only slightly greater than the value of 2.791 Å found in the free ligand. The distortion of the ligand found in **1**, and the unusual coordination geometry, therefore appears not to be due to a mismatch between the required 90° metal coordination angle and the preferred ligand bite angle, but is rather due to the steric effects of the phenyl substituents. The coordination of the ligands with the metal in the ligand planes would place the phenyl rings in the same region of space, and the coordination mode therefore distorts to avoid this clash. These observations are in stark contrast to the structural features of the tetrahedral complex [Zn(κ^2-Ph$_2$AFA)$_2$] (**2**), which is formed on treatment of ZnCl$_2$ with 2 equiv of NaPh$_2$AFA. The X-ray crystal structure of this complex (Figure 6) shows it to contain almost planar AFA ligands, with the maximum displacement of non-phenyl atoms from the C$_5$ mean plane of 0.074 Å. The maximum zinc displacement from the plane defined by the two ligand C═N bonds (ω, Figure 5) for the two inequivalent ligands is just 0.161 Å (cf. 1.27 Å in **1**). The intraligand N−N distances (3.304 and 3.305 Å) are substantially greater in **2** than in the free ligand and in **1**. Given the planarity of the ligands, it is surprising that the angles within the chelate ring are, in most cases, substantially greater than the corresponding angles in the free ligand, which is also planar. For example, the C−C−C angles at the two C$_5$ ring atoms contained within the chelate ring are 136.17°/135.58° and 136.05°/135.38° in the two independent ligands, which compares with 131.66°/131.87° in the free ligand and 131.33°/130.65° in the Pd complex (**1**). While these angles would not be expected to be 120° because of the constraints of the five-membered ring, they are considerably greater than 126°, which is predicted by simple geometry. The differences in the ligand coordination geometry between **1** and **2** may be accounted for by the fact that the tetrahedral coordination of the Zn(II) ion allows the phenyl substituents of one ligand to interdigitate with those of the other, while this is not possible in a square-planar complex.

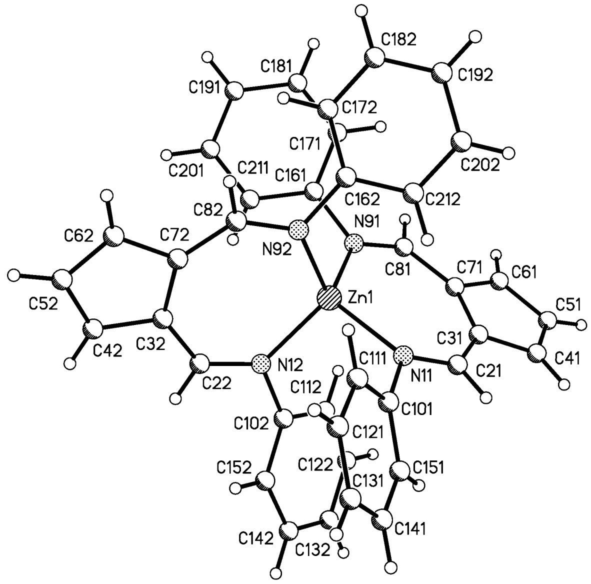

Figure 6. Molecular structure of [Zn(κ^2-Ph$_2$AFA)$_2$] (**2**). Selected bond lengths (Å) and angles (deg): Zn−N11 1.9962(16), N11−C21 1.313(2), C21−C31 1.411(3), C31−C71 1.459(3), C71−C81 1.410(3), C81−N91 1.132(2), Zn−N91 1.9981(16), N11−Zn−N91 111.62(6), Zn−N91−C81 127.75(13), N91−C81−C71 130.14(18), C81−C71−C31 135.58(18), C71−C31−C21 136.16(18), C31−C21−N11 129.99(18), C21−N11−Zn 127.68(13).

In an attempt to explore the ability of the Ph$_2$AFA ligand to act as an ambidentate ligand bonding to metals through both the diimine and C$_5$-ring donors, the zinc complex **2** was treated with [Cp*Ru(MeCN)$_3$][BF$_4$]. However, there is no zinc in the product isolated, the mass spectrum of which indicates it to be [Cp*Ru(Ph$_2$AFA)] (**3**). The X-ray crystal structure of **3** (Figure 7) shows that Ru coordination occurs via the C$_5$ ring of the AFA ligand. The fact that the [Cp*Ru]$^+$ fragment coordinates in this way rather than to the nitrogen donors is consistent with the known affinity of this species for π-aromatic ligands;[5]

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[11] Ammon, H. L.; Muller-Westerhoff, U. *Tetrahedron* **1974**, *30*, 1437.

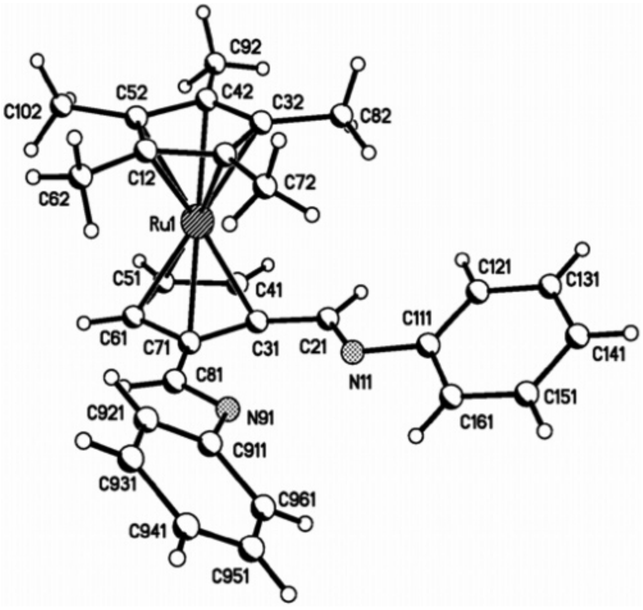

Figure 7. Molecular structure of [Cp*Ru(η^5-Ph$_2$AFA)] (**3**). Selected bond lengths (Å) and angles (deg): Ru−C31 2.168(7), Ru−C41 2.195(5), Ru−C51 2.222(4), Ru−C61 2.212(5), Ru−C71 2.160(6), N11−C21 1.312(6), C21−C31 1.402(8), C31−C71 1.442(6), C71−C81 1.482(9), C81−N91 1.293(6), N11−C21−C31 124.5(5), C21−C31−C71 131.9(7), C31−C71−C81 128.6(6), C71−C81−N91 123.7(4).

however, the possibility that the ligand is coordinated in this fashion due to the occupation of the nitrogen donors in **2** by zinc (which is subsequently lost on Ru coordination) cannot be discounted. An analogous 1,2-diiminoferrocene species has been prepared by condensation of 1,2-formylferrocene with aniline; however no structural data have been published.[12] There is a small difference between the C−C bond lengths from the ring to the imine carbon atoms, with C31−C21 being 0.081 Å shorter than C71−C81. There is also a smaller difference of 0.019 Å between the two C−N bonds, with C81−N91 being the shorter. These observations contrast with the indistinguishability of these pairs of bonds in the Pd complex **1**. There is therefore some evidence for a contribution from the fulvene form of the ligand (**A**, Figure 1) in **3**. The distances between the Ru center and the imine C atoms are 2.972 (C21) and 3.150 Å (C81), which is considerably longer than 2.282 Å found for the Ru−C bond to the exocyclic carbon atom in [CpRu(η^6-pentafulvene)][CF$_3$SO$_3$];[13] however C21 is the C atom indicated by C−C bond length data to have greater fulvene character, so there is perhaps some weak bonding between this C atom and the Ru center. The AFA ligand itself is not planar, the maximum deviation of non-Ph atoms from the C$_5$ plane being 0.34 Å (N11). The N−N separation is just 2.651 Å, shorter than in the free ligand, in which an N−H−N hydrogen bond is present.

The ^{1}H NMR spectrum of **3** at 293 K in CD$_2$Cl$_2$ contains two signals at 8.96 and 8.94 ppm, which may be assigned to the N═C−H protons. We initially attributed this inequivalence to the structurally observed Ru−C interaction with one of the imine carbon atoms and the observed coalescence of the two signals at 311 K to the fluxionality of this Ru−fulvene carbon interaction. However, the two N═CH carbon atoms are equivalent in the ^{13}C NMR spectrum, and the two ^{1}H signals are replaced by a singlet at 8.59 ppm on treatment of **3** with NaH. It therefore appears that the two nitrogen atoms in **3** are strongly basic and the location of a proton chelated by these two atoms accounts for the spectrum. The two signals for the C−H protons may therefore be assigned as a doublet (7 Hz) due to coupling to this added proton; consistent with this a broad triplet (7 Hz) is observed at 16.51 ppm (1H) for the chelated N−H−N proton. These NMR characteristics are similar to that found for the free ligand (Ph$_2$AFAH), in which these C−H protons occur as a doublet (7 Hz) at 8.29 ppm and the N−H−N triplet (7 Hz) is observed at 15.59 ppm in CD$_2$Cl$_2$. The source of the proton must be attributed to traces of water in the NMR solvent; however there is no evidence for the location of a proton in the region between the two nitrogen atoms in the X-ray structure of **3**, nor for a counteranion that this would necessitate. The anhydrous conditions under which **3** was crystallized therefore provides the neutral complex **3**. The high basicity of **3** may be accounted for by the ability of the two nitrogen atoms to chelate the added proton in a similar manner to that in well-known “proton-sponges” such as 1,8-bis(dimethylamino)naphthylene.[14] Indeed the hydrogen bonding and tautomerism in R$_2$AFAH systems have been subject to extensive investigations.[15] The equivalence of the two HC═N−Ph arms of the Ph$_2$AFA ligand in both **3** and its conjugate acid (**3**H$^+$) indicates that the Ru−C interaction with one of the imine carbon atoms observed in the solid-state structure is either absent in solution or subject to rapid fluxionality in which the Ru center interacts alternately with the two imine carbon atoms.

In contrast to the formation of **3**, treatment of the Pd complex **1** with 2 equiv of [Cp*Ru(MeCN)$_3$][BF$_4$] leads to a trimetallic complex, [Pd(Ph$_2$AFA)$_2$(RuCp*)$_2$][BF$_4$]$_2$ (**4**), in which the Pd atom has been retained. The X-ray crystal structure of **4** shows the complex to have an inversion center at the Pd atom, and both AFA ligands and Ru centers are therefore equivalent. The structure shows that the C$_5$ rings of both AFA ligands in the Pd complex **1** are now coordinated to [Cp*Ru]$^+$ units (Figure 8). The metrical parameters within the [Pd(Ph$_2$AFA)$_2$] part of the structure are similar to those observed in **1**, as discussed above. The coordination of the C$_5$ ring to Ru is again slightly asymmetric, with the bonds to the substituted ring atoms being slightly shorter. The angle between the PdN$_4$ plane and the mean plane defined by the two N═C imine bonds (θ, Figure 5) in **4** is 52.4°, similar to that in **1**, and the metal is displaced 1.107 Å from this plane (ω, Figure 5). The three C−H bonds of the C$_5$ ring of the AFA ligands are almost coplanar with the C$_5$ ring plane; however the two C−C bonds to the imine groups lie 0.283 Å (C81) and 0.352 Å (C21) below the plane (on the same side as the Ru atom). The differences between the chelate ring C−C bonds are not crystallographically significant and neither are those between the C−N bonds, and although the Ru distances to C21 (2.937 Å) and C71 (2.984 Å) are similar to that considered to be consistent with a weak interaction and a contribution from the fulvene form of the ligand in **3**, the C−C and C−N bond lengths in the chelate ring are not consistent

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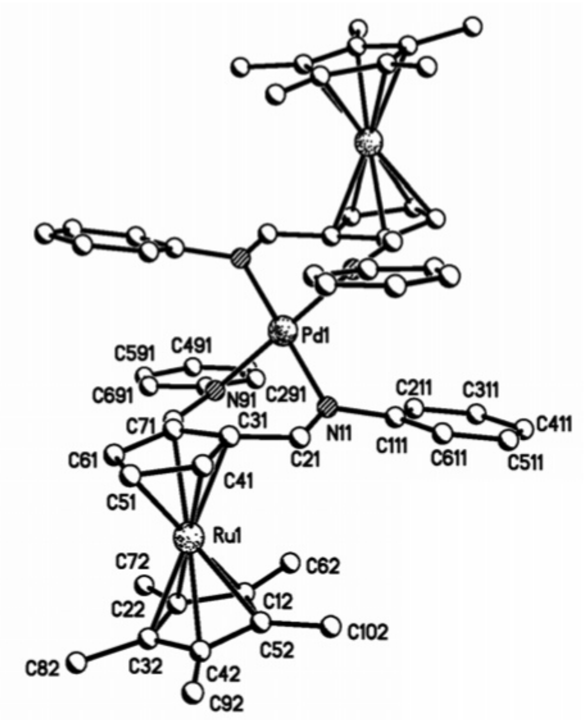


Figure 8. Molecular structure of the dication $[Pd(Ph_2AFA)_2(RuCp^*)_2]^{2+}$ (**4**). Selected bond lengths (Å) and angles (deg): Pd−N11 2.030(3), Pd−N91 2.034(3), N11−C21 1.296(5), C21−C31 1.434(5), C31−C71 1.472(5), C71−C81 1.430(5), C81−N91 1.290(5), Ru−C31 2.152(4), Ru−C41 1.299(4), Ru−C51 2.245(4), Ru−C61 1.191(4), Ru−C71 2.162(4), N11−C21 1.296(5), C21−C31 1.434(5), C31−C71 1.472(5), C71−C81 1.430(5), C81−N91 1.290(5), N11−C21−C31 124.5(5), C21−C31−C71 131.9(7), C31−C71−C81 128.6(6), C71−C81−N91 123.7(4).

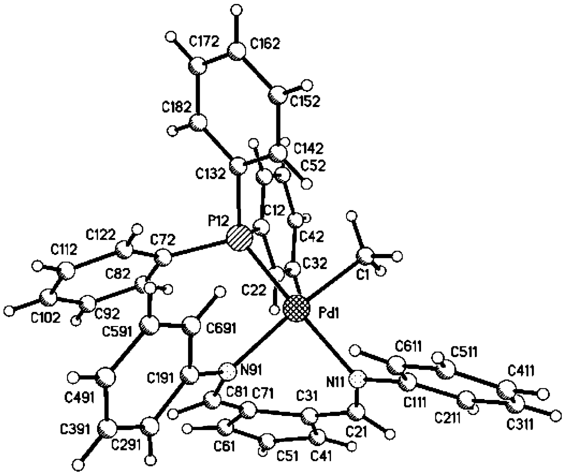


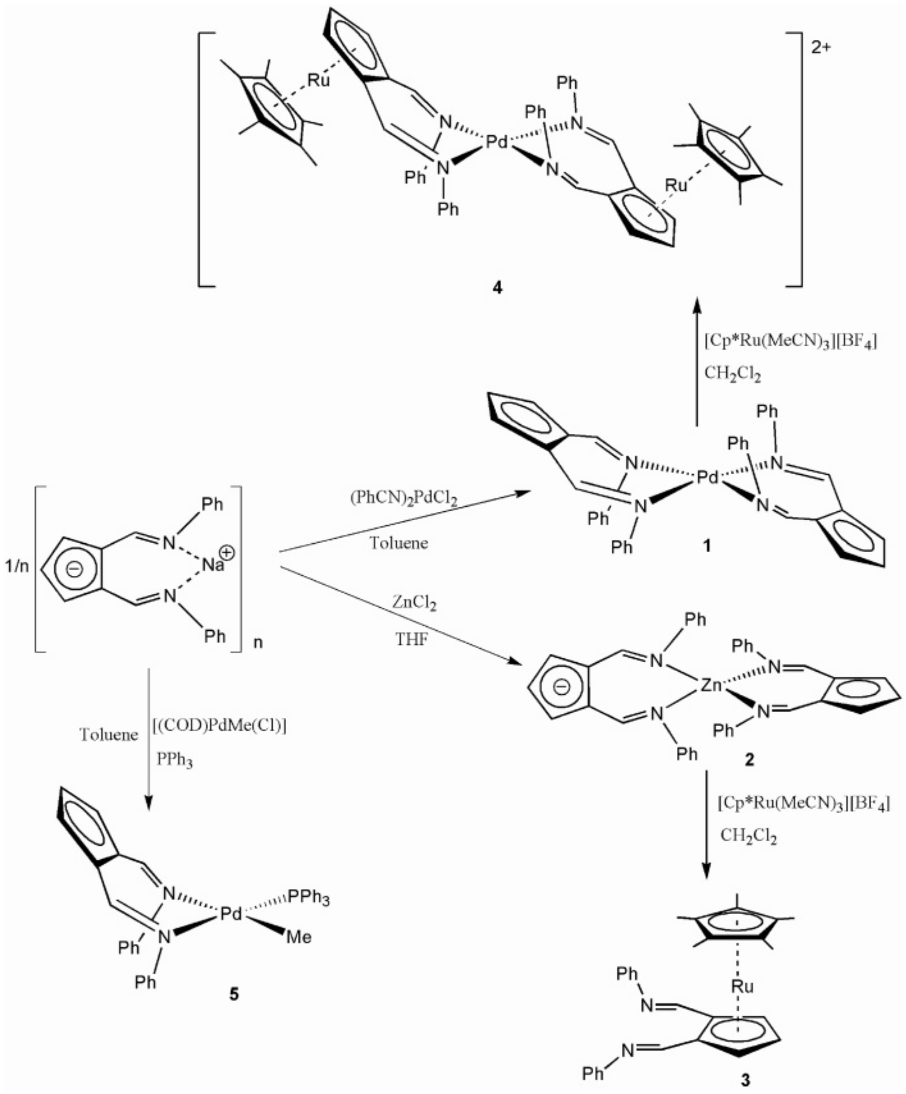
Figure 9. Molecular structure of $[(\kappa^2\text{-}Ph_2AFA)PdMe(PPh_3)]$ (**5**). Selected bond lengths (Å) and angles (deg): Pd−C1 2.0436(17), Pd−P 2.2157(5), Pd−N11 2.0945(15), Pd−N912.1335(14), N11−C21 1.300(2), C21−C31 1.424(2), C31−C71 1.459(3), C71−C81 1.405(3), C81−N91 (2), C31−C41 1.406(3), C41−C51 1.399(3), C51−C61 (3), C61−C71 1.416(2), N11−Pd−N91 87.62(6), C1−Pd−N11 87.24(7), C1−Pd−P 86.49(6), P−Pd−N91 97.95(4).

with this picture in **4**. Perhaps surprisingly, the coordination of the $[Cp^*Ru]^+$ fragments to the C_5 rings of the AFA ligands of **1** to provide **4** does not significantly affect the Pd−N bond distances (2.028/2.037 Å in **1** and 2.030/2.034 Å in **4**). This, coupled with the rather symmetrical η^5-bonding of the AFA C_5 rings to the Ru centers, suggests the electronic isolation of the two coordination sites in the ligand, thus indicating a predominant cyclopentadienyl−diimine form for the ligand (Figure 1, **B**).

An alkene polymerization catalyst of the type depicted in Figure 2 (**D**) requires a single AFA ligand coordinated to the metal, an alkyl ligand, and a labile neutral ligand to provide the site for alkene coordination. The ideal palladium precursor for this system would be a halide-bridged dimer of the form $[(\kappa^2\text{-}Ph_2AFA)Pd(\mu\text{-}X)]_2$, which could subsequently be methylated in a donor solvent to provide $[(\kappa^2\text{-}Ph_2AFA)PdMe(S)]$, or potentially the methyl-bridged dimer $[(\kappa^2\text{-}Ph_2AFA)Pd(\mu\text{-}Me)]_2$ in the absence of a donor. However, unfortunately all attempts to synthesize such a species from $PdCl_2$ or $[PdCl_2(NCR)_2]$ (R = Me, Ph) resulted only in the formation of the bis-chelate complex **1**. This is perhaps surprising given the steric hindrance present in **1**, which results in the unusual coordination mode of the ligands in this complex. The separation of the metal centers by the bridging halides in the dimeric system would relieve this problem even though the two ligands would occupy the same plane. Nevertheless, we have been able to prepare a complex containing a single Ph_2AFA ligand by treating [(COD)PdMe(Cl)] with $NaPh_2AFA$ in the presence of PPh_3, which provides the complex $[(\kappa^2\text{-}Ph_2AFA)PdMe(PPh_3)]$ (**5**). The X-ray crystal structure of **5** (Figure 9) shows the Ph_2AFA ligand again to adopt the "side-on" type of coordination mode, on this occasion induced by the steric bulk of the coordinated PPh_3 ligand. The steric interaction between the PPh_3 ligand and the phenyl substituent of the Ph_2AFA ligand is indicated by the large P−Pd−N angle of 97.95(4)°; all of the other coordination angles at Pd are substantially less than 90° to compensate. This interaction also results in the PPh_3 ligand lying substantially out of the square plane of the complex, the P atom being 0.551 Å out of the mean plane defined by the other three donor atoms, which are effectively coplanar with the metal. The Pd−N bond trans to the methyl ligand [2.1335(14) Å] is substantially longer than that trans to the phosphine [2.0945(15) Å], reflecting the greater trans-influence of the alkyl. This longer bond is also that cis to the PPh_3 ligand, so steric effects may also make a contribution to this difference in Pd−N bond distances. Both of these Pd−N bonds are significantly longer than in the other Pd complexes (**1** and **4**), which presumably reflects the extreme distortion of the ligand coordination geometry forced by the bulk of the PPh_3 ligand. The angle between the mean plane of the square-planar Pd coordination environment and that defined by the two N═C imine bonds (θ, Figure 5) in **5** is 72.5°, and the palladium center is displaced 1.393 Å from this plane (ω, Figure 5). The plane of the C_5 ring is almost perpendicular to the metal square plane (85.1°). The distortion of the Ph_2AFA ligand coordination geometry is therefore even more extreme in this complex than in either **1** or **4**. The ^1H NMR spectrum of **5** shows a rather large coupling of one of the imino protons with the phosphorus of the PPh_3 ligand (J = 8.34 Hz), also confirmed by H−P correlated NMR experiments. Coupling with the phosphorus is also observed for the methyl group, which appears as a doublet at −0.06 ppm with a coupling constant of 3.65 Hz.

Reactivity toward Ethylene. We have undertaken preliminary studies of the reactivity of **5** toward ethylene at low pressure. The methyl complex **5** showed no reactivity toward ethylene (5 bar, 25 and 50 °C) in toluene solution; however this is not unexpected given the coordinative saturation of the complex provided by the PPh_3 ligand. For neutral nickel(II)-based ethylene polymerization catalysts $[Ni(COD)_2]$ has been used as an effective phosphine scavenger,[16] and the addition of

Scheme 1. Synthetic Routes to the Ph_2AFA Complexes Reported



2 molar equiv of this complex to a solution of **5** in toluene solution provided a system that showed some reactivity toward ethylene. Under the same reaction conditions $[Ni(COD)_2]$ alone showed no reactivity toward ethylene. Both linear polyethylene ($M_n = 8400$, $M_w = 140\,000$, PDI $= 17$) and a mixture of oligomers up to C_{44} were produced by the system. However, the activity is extremely low [0.02 $kg(mol{\cdot}h{\cdot}atm)^{-1}$ for the polymer], and the formation of both polymer and oligomers and the broad molecular weight distribution of the former indicate the presence of more than one active species. A full description of the details of this system will need to await further work, and we hope to report on this in the near future.

Conclusions

The synthetic routes to the complexes reported are shown in Scheme 1. The ability of the Ph_2AFA ligand to coordinate to metals in such a wide range of geometries is unprecedented for a chelating diimine ligand, which normally favors complexation of the metal within the plane of the ligand.[17] This must be a result of the 1,4-relationship of the imine donors within the AFA ligand framework, which contrasts with the more common 1,2-diimine systems, and the electronic flexibility conferred by the availability of the fulvene form of the ligand (Figure 1, **A**). The almost symmetric coordination of the Cp^*Ru^+ unit to the C_5 ring of the $[Ph_2AFA]^-$ ligand, when the nitrogen donors are either occupied or vacant, indicates the presence of significant charge within the C_5 ring of the AFA ligand. The slight bond alternation within the N−C−C−C−C−N portion of the ligand in **3** and the apparent interaction between the Ru center and the fulvene carbon atom thus implied provide evidence for a contribution from the fulvene form of the ligand (Figure 1, **A**) in this complex. However this is absent in **4**, where the nitrogen atoms are Pd coordinated. The AFA ligand system thus appears to be rather flexible, both sterically and electronically, capable of providing either a bis-imino or imino-amido donor at the nitrogen sites and either a cyclopentadienyl or fulvene donor at the C_5 ring site, along with exceptional flexibility of coordination geometry at the nitrogen donor sites. This suggests that the ligand should be compatible with a wide range of metals in a variety of oxidation states and be capable of accommodating a range of metal steric environments. The identity of the species active in oligomerization and polymerization of ethene formed on activation of **5** with $[Ni(COD)_2]$ remains to be characterized, and our work in this area continues.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **1**, **2**, **3**, **4**, and **5**; ^{13}C NMR spectra for compounds **1** and **3**; mass spectrum of the oligomer mixture obtained on activation of **5** with [Ni(COD)$_2$] and treatment with ethylene; and the gel permeation chromatogram of the polyethylene also obtained from this system. This material is available free of charge via the Internet at http://pubs.acs.org.

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