Anionic Phosphinimine-Chelate Complexes of Rhodium and Iridium: Steric and Electronic Influences on Oxidative Addition of CH_2Cl_2

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Received July 16, 2003

The phosphinimines Ph_3PNR (R = Ph **1**, 2,6-$Me_2C_6H_3$ **2**, 3,5-$Me_2C_6H_3$ **3**, 2,6-*i*-$Pr_2C_6H_3$ **4**) were prepared and used to generate the species of the form $[Li(o\text{-}C_6H_4PPh_2NR)]_2{\cdot}Et_2O$ (R = Ph **5**, 2,6-$Me_2C_6H_3$ **6**, 3,5-$Me_2C_6H_3$ **7**, 2,6-*i*-$Pr_2C_6H_3$ **8**). Subsequent reactions with $[Rh(\mu\text{-}Cl)(COD)]_2$ gave the complexes $Rh(COD)(o\text{-}C_6H_4PPh_2NR)$ (R = Ph **9**, 2,6-$Me_2C_6H_3$ **10**, 3,5-$Me_2C_6H_3$ **11**, 2,6-*i*-$Pr_2C_6H_3$ **12**). Similarly, the Ir analogue of **9** (**13**) was prepared using $[Ir(\mu\text{-}Cl)(COD)]_2$. The reaction of **9** with $(CH_2PPh_2)_2$ afforded $Rh(PPh_2CH_2CH_2PPh_2)(o\text{-}C_6H_4PPh_2NPh)$ (**14**). Compound **9** was also shown to react with CH_2Cl_2 to give two products, one of which was confirmed to be $[Rh(o\text{-}C_6H_4PPh_2NPh)(CH_2\text{-}o\text{-}C_6H_4PPh_2NPh)(\mu\text{-}Cl)_2Rh(COD)]$ (**15**). Similar treatment of **10** and **12** with CH_2Cl_2 showed no reaction, while reaction of **11** with CH_2Cl_2 gave a mixture of unidentified products. The related imidazole-phosphinimine ligands $(N_2C_3H_3)PPh_2NR$ (R = Ph **18**, 2,6-$Me_2C_6H_3$ **19**) were also prepared. These ligands react with NaH to give the corresponding Na-imidazolate-phosphinimines, **20** and **21**, and subsequent reaction with $[Rh(\mu\text{-}Cl)(COD)]_2$ gave the complexes $Rh(COD)((N_2C_3H_2)PPh_2NR)$ (R = Ph **22**, 2,6-$Me_2C_6H_3$ **23**). The compounds **22** and **23** do not react with CH_2Cl_2. The effects of steric and electronic modifications to the ligands on oxidative addition of C−Cl bonds are discussed. DFT calculations were performed on the model fragments $[Rh((C_6H_4)PH_2NH)]$ and $[Rh((N_2C_3H_2)PH_2NH)]$, and the calculated atomic charges provide some insight into the reactivity of these compounds.

Introduction

The oxidative addition of alkyl-halides, in particular alkyl-chlorides, has attracted much academic attention as a result of the applications of this reaction in industrial processes. Nonetheless, of the known oxidative reactions of CH_2Cl_2 to Rh, the majority afford Rh(III) products in which $RhCl(CH_2Cl)$ fragments are seen.[1−7] As an example, the species Rh(I) precursor $[Rh(Me_2bipy)(DMSO)_2]^+$ was shown to react with CH_2Cl_2 to give $[RhCl(Me_2bipy)(DMSO)_2(CH_2Cl)]^+$.[8] Alternatively, oxidative addition to Rh dimers has led to the formation of methylene-bridged species.[9,10] One such example is $(RhCl(dppe)(\mu\text{-}Cl))_2(\mu\text{-}CH_2)$.[10] In rare cases, oxidative addition of CH_2Cl_2 is followed by insertion into the Rh−L bond.[7,11] Such is the case in the formation of $(Me_3P)_3RhCl_2(CH_2PMe_3)$[12] and $RhCl_2(CH_2P((N(CH_2CH_2N)(CH_2CH_2)_2NH)(PPh_3)$.[13]

Recently a number of groups have been probing the utility of diimine (C═NR) and related late metal complexes in olefin polymerization catalysis.[14−27] As our

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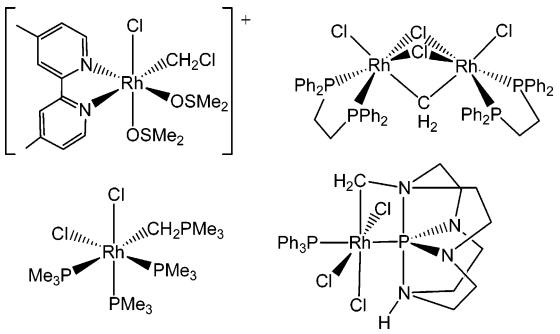
10.1021/om030539g CCC: $27.50
Publication on Web 12/25/2003

group has had success in developing early transition metal polymerization catalysts based on phosphinimide ligands,[28,29] we have initiated a program examining a variety of related phosphinimine-based ligands (P═NR) for late metal chemistry. In a recent work, we described



the development of phosphinimine-pyridine and phosphinimine-imidazole chelate complexes of Fe and Ni.[30] While these complexes provided only modestly active ethylene oligomerization calatysts, the insight garnered from DFT computations infers that inclusion of the P−N fragment into the ligand results in increased nucleophilicity of the metal center. While this characteristic weakens ethylene−metal interactions, it should in principle enhance oxidative addition reactions. In this paper, we describe the preparation of Rh and Ir complexes of *ortho*-metalated phenyl-phosphinimine and imidazolate-phosphinimine ligands. In some cases, these species undergo oxidative addition of CH_2Cl_2, resulting in C−C bond formation via insertion into the Rh−aryl-C bond. However, steric congestion or electronic perturbations to the ligand are shown to inhibit this reaction. These experimental results are considered and discussed in the light of DFT calculations.

Experimental Section

General Data. All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and either a Vacuum Atmospheres or Innovative Technolgies inert atmosphere glovebox. Solvents were purified employing a Grubbs type solvent purification system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C_6D_6 at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references, and chemical shifts are reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. Combustion analyses were done in-house employing a Perkin-Elmer CHN analyzer. Ph_3PNPh (**1**) and $[M(\mu\text{-Cl})(COD)]_2$ (M = Rh, Ir; COD = cyclooctadiene) were purchased from the Aldrich Chemical Co. The compounds Li-$(Et_2O)C_6H_4Ph_2PNPh$ (**5**) and $(N_2C_3H_3)PPh_2$ (**17**) were generated with minor modifications to published methods.[30−32]

Synthesis of Ph_3PNR (R = 2,6-$Me_2C_6H_3$ (2), 3,5-$Me_2C_6H_3$ (3), 2,6-*i*-$Pr_2C_6H_3$ (4)). Compounds **2**−**4** were prepared by similar methods; thus only one representative procedure is described. A solution of 2,6-$Me_2C_6H_3N_3$ (1.2 g, 9.9 mmol) in CH_2Cl_2 (2 mL) was added dropwise at 25 °C to a solution of PPh_3 (1.3 g, 4.9 mmol) in the same solvent (5 mL). The homogeneous solution was stirred overnight and was then concentrated to approximately 2 mL in vacuo. Pentane (5 mL) was added, and a pale yellow solid precipitated out of solution. The product was filtered, washed with cold pentane (3 × 5 mL), and dried in vacuo. Yield: 1.12 g (64%). **2**: ^1H NMR δ 7.64−7.71 (m, 6H, PPh_3), 7.14−7.16 (m, 2H, $Me_2C_6H_3$), 7.10−7.14 (m, 9H, PPh_3), 6.86−6.91 (m, 1H, $Me_2C_6H_3$), 2.24 (s, 6H, $Me_2C_6H_3$); $^{13}C\{^1H\}$ NMR δ 148.4 (s), 135.5 (s), 133.6 (d, $^2J_{P-C}$ = 78 Hz), 133.2 (s), 133.9 (d, $^3J_{P-C}$ = 10 Hz), 131.5 (d, $^4J_{P-C}$ = 3 Hz), 128.1−128.8 (m, obscured by C_6D_6), 119.5 (d, $^4J_{P-C}$ = 3 Hz), 21.8 (s); $^{31}P\{^1H\}$ NMR δ −9.8 (s). Anal. Calcd for $C_{26}H_{24}$-PN: C, 81.87; H, 6.34; N, 3.67. Found: C, 81.46; H, 6.41; N, 3.49. **3**: Yield 1.02 g (70%); ^1H NMR δ 7.80−7.87 (m, 6H, PPh_3), 6.93−7.06 (m, 9H, PPh_3), 6.93 (s, 2H, $Me_2C_6H_3$), 6.48 (s, 1H, $Me_2C_6H_3$), 2.19 (s, 6H, $Me_2C_6H_3$); $^{13}C\{^1H\}$ NMR δ 152.2 (s), 138.2 (s), 133.3 (d, $^2J_{P-C}$ = 10 Hz), 133.1 (d, $^2J_{P-C}$ = 98 Hz), 131.7 (d, $^4J_{P-C}$ = 2 Hz), 128.1−129.0 (m, obscured by C_6D_6), 122.2 (d, $^3J_{P-C}$ = 18 Hz), 120.2 (s), 21.3 (s); $^{31}P\{^1H\}$ NMR δ −1.5 (s). Anal. Calcd for $C_{26}H_{24}PN$: C, 81.87; H, 6.34; N, 3.67. Found: C, 81.53; H, 6.19; N, 3.39. **4**: Yield 1.34 g (80%); ^1H NMR δ 7.61−7.69 (m, 6H, PPh_3), 7.14−7.22 (m, 3H, *i*-$Pr_2C_6H_3$), 6.95−7.08 (m, 9H, PPh_3), 3.67 (sept, 2H, $^3J_{H-H}$ = 7 Hz, *i*-Pr), 1.09 (d, 12H, $^3J_{H-H}$ = 7 Hz, *i*-Pr); $^{13}C\{^1H\}$ NMR δ 145.1 (s), 143.3 (d, $^1J_{P-C}$ = 7 Hz), 134.3 (d, $^2J_{P-C}$ = 101 Hz), 133.0 (d, $^3J_{P-C}$ = 9 Hz), 131.7 (d, $^4J_{P-C}$ = 2 Hz), 128.2−128.9 (m, obscured by C_6D_6), 123.6 (s), 120.4 (d, $^4J_{P-C}$ = 3 Hz), 29.4 (s), 24.3 (s); $^{31}P\{^1H\}$ NMR δ −8.9 (s). Anal. Calcd for $C_{30}H_{32}$-PN: C, 82.35; H, 7.37; N, 3.20. Found: C, 82.46; H, 7.42; N, 3.19.

Generation of $[Li(o\text{-}C_6H_4Ph_2PNR)]_2(Et_2O)$ (R = Ph (5), 2,6-$Me_2C_6H_3$ (6), 3,5-$Me_2C_6H_3$ (7), 2,6-*i*-$Pr_2C_6H_3$ (8)). These compounds were prepared in a similar fashion although the Li reagent and time of reactions varied. One preparation is detailed, and variations for the others are indicated. Compound **2** (0.2 g, 0.52 mmol) was dissolved in Et_2O (5 mL), and LiMe (0.45 mL, 0.63 mmol) was added dropwise at 25 °C. The solution turned yellow immediately and gradually changed color to light orange. The mixture was stirred overnight, after which time the solvent was removed in vacuo. **5**: LiPh, overnight, yield 0.16 g (47%); ^1H NMR δ 8.28 (d, 1H, $^3J_{H-H}$ = 7 Hz, PC_6H_4), 7.89 (m, 4H, PPh_2), 7.28 (m, 2H, NPh), 7.09−6.95 (m, 7H), 6.89−6.94 (m, 4H, PPh_2), 6.61 (m, 1H, PC_6H_4), 3.35−3.31 (m, 2H, CH_2), 1.15 (m, 3H, CH_2Me); $^{13}C\{^1H\}$ NMR δ 151.7 (s), 142.1 (s), 133.4 (d, $^2J_{P-C}$ = 9 Hz), 132.5 (s), 131.5 (s), 130.8 (s), 129.5−129.8 (m), 128.5−128.8 (m), 123.9−124.5 (m), 123.3 (s), 117.9 (s), 65.6 (s), 14.9 (s); $^7Li\{^1H\}$ NMR δ 4.2 (s); $^{31}P\{^1H\}$ NMR δ 18.1 (s). **6**: Yield 0.18 g (85%); ^1H NMR δ 8.51 (br, 1H, PC_6H_4), 7.51−7.54 (m, 4H, PPh_2), 7.28 (br, 1H, $Me_2C_6H_3$), 7.00−7.04 (m, 4H, PPh_2), 6.93−6.96 (m, 6H), 6.79−6.81 (m, 1H, PC_6H_4), 3.08−3.12 (m, 2H, CH_2), 1.96 (s, 6H, $Me_2C_6H_3$), 0.85−0.90 (m, 3H, CH_2Me); $^{13}C\{^1H\}$ NMR δ 147.8 (s), 141.9 (s), 141.2 (s), 134.5 (d, $^1J_{P-C}$ = 7 Hz), 133.2 (s), 132.7 (d, $^2J_{P-C}$ = 8 Hz), 131.6 (s), 130.2 (s), 128.7 (s), 123.4 (s), 120.5 (s), 65.1 (s), 20.7 (s), 14.5 (s); $^7Li\{^1H\}$ NMR δ 3.38 (s); $^{31}P\{^1H\}$ NMR δ 15.2 (s). **7**: BuLi, overnight, yield 0.13 g (63%); ^1H NMR δ 8.28 (br, 1H, PC_6H_4), 7.75−7.85 (m, 4H, PPh_2), 7.26−

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7.32 (m, 1H, PC_6H_4), 7.18 (m, 1H, PC_6H_4), 6.93−7.08 (m, 8H), 6.35−6.36 (m, 2H, $Me_2C_6H_3$), 2.82 (br, 2H, CH_2), 1.97−2.10 (m, 6H, $Me_2C_6H_3$), 0.49 (br, 3H, CH_2Me); $^{13}C\{^1H\}$ NMR δ 151.7 (s), 144.9 (s), 142.2 (s), 138.6 (s), 137.8 (s), 134.1 (d, $^2J_{P-C} = 9$ Hz), 133.3 (s), 132.8 (s), 131.4 (s), 131.2 (s), 130.4 (s), 122.9 (s), 65.9 (s), 21.9 (s), 14.7 (s); $^7Li\{^1H\}$ NMR δ: 4.21 (s); $^{31}P\{^1H\}$ NMR δ 17.9 (s). **8**: LiMe, 12 days at 25 °C; yield 0.14 g (52%); ^1H NMR δ 8.61 (d, 1H, $^3J_{H-H} = 7$ Hz, PC_6H_4), 7.48−7.51 (m, 4H, PPh_2), 7.23−7.25 (m, 2H, *i*-$Pr_2C_6H_3$), 6.89−7.10 (m, 10H, PPh_2), 3.65 (sept, 2H, $^3J_{H-H} = 7$ Hz, *i*-Pr), 3.21−3.27 (m, 2H, CH_2), 1.22 (br, 6H, *i*-Pr), 1.06−1.10 (m, 3H, CH_2Me), 0.57 (br, 6H, *i*-Pr); $^{13}C\{^1H\}$ NMR δ 145.2 (d, $^1J_{P-C} = 7$ Hz), 144.6 (s), 142.7 (d, $^1J_{P-C} = 7$ Hz), 134.4 (s), 133.1 (d, $^2J_{P-C} = 8$ Hz), 132.4 (d, $^2J_{P-C} = 9$ Hz), 130.9 (s, PPh_2), 130.6 (s), 124.3 (s), 123.5 (s), 122.3 (s), 119.9 (s), 65.7 (s), 28.9 (s), 23.8 (s), 15.3 (s); $^7Li\{^1H\}$ NMR δ 6.73 (s); $^{31}P\{^1H\}$ NMR δ 18.4 (s).

Synthesis of Rh(COD)(*o*-$C_6H_4PPh_2NR$), R = Ph (9), 2,6-$Me_2C_6H_3$ (10), 3,5-$Me_2C_6H_3$ (11), 2,6-*i*-$Pr_2C_6H_3$ (12), and Ir(COD)(*o*-$C_6H_4PPh_2NPh$) (13). Compounds **9**−**13** were prepared by similar methods; thus only one representative procedure is described. A mixture of **6** (0.26 g, 0.31 mmol) and $[Rh(\mu\text{-Cl})(COD)]_2$ (0.22 g, 0.44 mmol) was dissolved in THF (5 mL) at 25 °C. The homogeneous reddish solution was stirred overnight, after which the solvent was removed in vacuo. The residue was washed with pentane and recrystallized from THF/Et_2O or THF/C_6H_6. **9**: Yield 0.24 g (60%); ^1H NMR δ 7.61−7.67 (m, 4H, PPh_2), 7.53−7.55 (m, 1H, PC_6H_4), 7.18−7.24 (m, 1H, PC_6H_4), 6.98−7.06 (m, 4H, PPh_2), 6.95−6.96 (m, 2H, NPh), 6.84−6.92 (m, 6H), 6.74−6.79 (m, 1H, PC_6H_4), 4.36−4.39 (m, 2H, COD), 4.13−4.16 (m, 2H, COD), 2.50−2.60 (m, 2H, COD), 2.36−2.46 (m, 2H, COD), 2.02−2.11 (m, 2H, COD), 1.91−1.98 (m, 2H, COD); $^{13}C\{^1H\}$ NMR δ 174.0 (d, $^1J_{Rh-C} = 40$ Hz), 148.1 (d, $^2J_{P-C} = 4$ Hz), 140.1 (s), 133.1 (d, $^2J_{P-C} = 9$ Hz), 131.6 (s), 129.9 (s), 129.7 (s), 129.4 (s), 129.3 (s), 128.5 (s), 123.4 (s), 122.9 (s), 93.4 (d, $^1J_{Rh-C} = 7$ Hz), 68.9 (d, $^1J_{Rh-C} = 15$ Hz), 32.5 (s), 30.7 (s); $^{31}P\{^1H\}$ NMR δ 46.4 (d, $^2J_{Rh-P} = 10$ Hz). Anal. Calcd for $C_{32}H_{31}PNRh$: C, 68.21; H, 5.55; N, 2.49. Found: C, 68.27; H, 5.71; N, 2.67. **10**: Yield 0.08 g (43%); ^1H NMR δ 7.56−7.60 (m, 4H, PC_6H_4), 7.25 (d, 1H, $^3J_{H-H} = 7$ Hz, PC_6H_4), 6.82−6.96 (m, 11H), 4.17−4.18 (m, 2H, COD), 3.94−3.95 (m, 2H, COD), 2.54−2.56 (m, 2H, COD), 2.36−2.38 (m, 2H, COD), 2.12 (s, 6H, $Me_2C_6H_3$), 2.04−2.07 (m, 2H, COD), 1.91−1.94 (m, 2H, COD); $^{13}C\{^1H\}$ NMR δ 173.5 (d, $^1J_{Rh-C} = 41$ Hz), 145.4 (s), 136.5 (s), 135.5 (s), 132.8 (d, $^2J_{P-C} = 9$ Hz), 131.1 (s), 130.9 (s), 129.9 (s), 129.8 (s), 129.6 (s), 128.2 (s) 123.9 (br), 94.4 (d, $^1J_{Rh-C} = 7$ Hz), 68.8 (d, $^1J_{Rh-C} = 15$ Hz), 32.3 (s), 30.0 (s), 20.9 (s); $^{31}P\{^1H\}$ NMR δ 43.3 (d, $^2J_{Rh-P} = 11$ Hz). Anal. Calcd for $C_{34}H_{35}PNRh$: C, 69.04; H, 5.96; N, 2.37. Found: C, 68.61; H, 5.70; N, 2.28. **11**: ^1H NMR δ 7.65−7.69 (m, 4H, PPh_2), 7.55 (d, 1H, $^3J_{H-H} = 7$ Hz, C_6H_4), 7.23 (d, 1H, $^3J_{H-H} = 7$ Hz, C_6H_4), 7.04 (d, 1H, $^3J_{H-H} = 7$ Hz, C_6H_4), 6.98−7.00 (m, 2H, PPh_2), 6.88−6.93 (m, 5H), 6.65 (s, 2H, C_6H_3), 6.47 (s, 1H, C_6H_3), 4.46−4.48 (m, 2H, COD), 4.14−4.16 (m, 2H, COD), 2.55−5.58 (m, 2H, COD), 2.42−2.44 (m, 2H, COD), 2.06−2.08 (m, 2H, COD), 2.00−2.02 (m, 2H, COD), 1.97 (s, 6H, Me); $^{13}C\{^1H\}$ NMR δ 174.2 (d, $^1J_{Rh-C} = 40$ Hz), 147.9 (s), 141.9 (s), 137.5 (s), 135.4 (d, $^2J_{P-C} = 18$ Hz), 133.5 (d, $^1J_{P-C} = 9$ Hz), 131.7 (s), 130.3 (s), 130.0 (s), 128.6 (s), 128.4 (s), 127.4 (d, $^3J_{Rh-C} = 7$ Hz), 125.1 (s), 123.4 (s), 93.8 (d, $^1J_{Rh-C} = 7$ Hz), 69.1 (d, $^1J_{Rh-C} = 15$ Hz), 32.6 (s), 30.1 (s), 21.4 (s); $^{31}P\{^1H\}$ NMR δ 47.6 (s). Anal. Calcd for $C_{34}H_{35}PNRh$: C, 69.04; H, 5.96; N, 2.37. Found: C, 69.00; H, 5.59; N, 2.24. **12**: Yield 0.08 g (43%); ^1H NMR δ 7.74−7.78 (m, 4H, PPh_2), 7.51 (d, 1H, $^3J_{Rh-H} = 8$ Hz, PC_6H_4), 7.19 (s, 1H, PC_6H_4), 6.99−7.02 (m, 4H, PPh_2), 6.93−6.97 (m, 2H, *i*-$Pr_2C_6H_3$), 6.86−6.92 (m, 5H), 4.18−4.21 (m, 4H, COD), 2.41−2.54 (m, 4H, COD), 1.96−2.01 (m, 4H, COD), 1.52 (d, 6H, $^3J_{H-H} = 7$ Hz, *i*-Pr), 0.40 (d, 6H, $^3J_{H-H} = 7$ Hz, *i*-Pr); $^{13}C\{^1H\}$ NMR δ 173.6 (d, $^1J_{Rh-C} = 40$ Hz), 146.5 (d, $^1J_{P-C} = 6$ Hz), 143.0 (d, $^1J_{P-C} = 5$ Hz), 140.3 (s), 135.5 (d, $^2J_{Rh-C} = 18$ Hz), 132.7 (d, $^2J_{P-C} = 8$ Hz), 131.4 (s), 131.3 (s), 130.3 (s), 129.6 (s), 129.4 (s), 124.1 (s), 123.8 (d, $^3J_{P-C} = 3$ Hz), 123.3 (s), 123.1 (s); $^{31}P\{^1H\}$ NMR δ 39.9. Anal. Calcd for $C_{38}H_{43}PNRh$: C, 70.47; H, 6.69; N, 2.16. Found: C, 70.34; H, 6.54; N, 2.01. **13**: Yield 0.06 g (67%); ^1H NMR δ 7.85 (d, 1H, $^3J_{P-H} = 9$ Hz, PC_6H_4), 7.53−7.60 (m, 4H, PPh_2), 7.25−7.30 (m, 1H, PC_6H_4), 7.07−7.11 (m, 2H, NPh), 6.90−6.98 (m, 6H), 6.81−6.87 (m, 4H, PPh_2), 6.73−6.78 (m, 1H, PC_6H_4), 3.82−3.99 (m, 4H, COD), 2.35−2.61 (m, 4H, COD), 1.82−1.99 (m, 4H, COD); $^{13}C\{^1H\}$ NMR δ 172.9 (s), 146.3 (s), 140.9 (s), 135.5 (s), 133.2 (d, $^2J_{P-C} = 9$ Hz), 133.1 (s), 130.4 (s), 130.1 (s), 129.8 (s), 129.5 (s), 124.3 (s), 123.9 (s), 77.8 (s), 52.7 (s), 33.3 (s), 31.4 (s); $^{31}P\{^1H\}$ NMR δ 57.7 (s). Anal. Calcd for $C_{32}H_{31}PNIr$: C, 58.88; H, 4.79; N, 2.15. Found: C, 58.69; H, 4.77; N, 2.05.

Synthesis of Rh($PPh_2CH_2CH_2PPh_2$)(*o*-$C_6H_4PPh_2NPh$) (14). To a solution of **9** (0.03 g, 0.08 mmol) in THF (5 mL) was added dropwise a solution of 1,2-bis(diphenylphosphinoethane) (0.04 g, 0.07 mmol) in THF (5 mL). The mixture was stirred overnight at 25 °C, and the solvent was then removed in vacuo. The resulting solid was washed with benzene and was subsequently dried in vacuo. Yield: 0.03 g (51%); ^1H NMR δ 7.99−8.03 (m, 4H, PPh_2), 7.74 (br, 1H, PC_6H_4), 7.53−7.57 (m, 4H, PPh_2), 7.48−7.51 (m, 4H, PPh_2), 7.02−7.08 (m, 15H), 6.93−6.99 (m, 6H), 6.81 (t, 1H, $^3J_{H-H} = 7$ Hz, PC_6H_4), 6.70 (dd, 1H, $^3J_{P-H} = 13$ Hz, $^3J_{H-H} = 6$ Hz, PC_6H_4), 6.53−6.56 (m, 2H, NPh), 6.45−6.48 (m, 1H, PC_6H_4), 1.83−1.93 (m, 2H, CH_2), 1.64−1.73 (m, 2H, CH_2); $^{13}C\{^1H\}$ NMR δ 153.9 (s), 146.3 (s), 144.6 (s), 142.2 (br), 138.6 (d, $^2J_{P-C} = 24$ Hz), 137.9 (d, $^2J_{P-C} = 23$ Hz), 134.4 (d, $^1J_{P-C} = 33$ Hz), 133.6 (d, $^2J_{P-C} = 11$ Hz), 132.5 (s), 131.4 (s), 130.9 (s), 128.7 (s), 126.2 (d, $^2J_{P-C} = 13$ Hz), 123.5 (s), 121.1 (d, $^2J_{P-C} = 15$ Hz), 119.2 (s), 32.1 (br), 29.4 (br); $^{31}P\{^1H\}$ NMR δ 74.9 (dd, $^1J_{Rh-P} = 104$ Hz, $^2J_{P-P} = 24$ Hz), 57.2 (ddd $^1J_{Rh-P} = 121$ Hz, $^2J_{P-P} = 25$ Hz, $^3J_{P-P} = 11$ Hz), 24.1 (dd, $^2J_{Rh-P} = 24$ Hz, $^3J_{P-P} = 11$ Hz). Anal. Calcd for $C_{50}H_{43}P_3NRh$: C, 70.34; H, 5.08; N, 1.64. Found: C, 69.95; H, 5.38; N, 1.55.

Synthesis of [Rh(*o*-$C_6H_4PPh_2NPh$)(CH_2-*o*-$C_6H_4PPh_2NPh$)-(μ-Cl)$_2$Rh(COD)] (15). Compound **9** (0.098 g, 0.17 mmol) was dissolved in CH_2Cl_2 (10 mL) and heated at reflux for 24 h, during which time the solution became orange. The solvent was removed in vacuo, and the product was recrystallized in benzene/CH_2Cl_2 following filtration. Yield: 0.18 g (94%); ^1H NMR δ 8.40 (br, 2H, P(C_6H_4)), 7.97 (dd, 1H, $^3J_{Rh-H} = 8$ Hz, $^4J_{P-H} = 3$ Hz, P(C_6H_4)), 7.87−7.92 (m, 4H, PPh_2), 7.79−7.84 (m, 2H, P(C_6H_4)), 7.65−7.69 (m, 3H, P(C_6H_4)), 7.45−7.53 (m, 4H, PPh_2), 7.28 (t, 2H, $^3J_{H-H} = 7$ Hz, NPh), 6.83−7.13 (m, 16H), 6.68−6.76 (m, 4H, NPh), 4.23 (dd, 2H, $^2J_{Rh-H} = 10$ Hz, $^4J_{P-H} = 4$ Hz, $RhCH_2$), 4.10−4.12 (m, 2H, COD), 3.78−3.80 (m, 2H, COD), 2.21−2.26 (m, 4H, COD), 1.33−1.37 (m, 4H, COD); $^{13}C\{^1H\}$ NMR δ 170.7 (m), 157.9 (s), 150.9 (s), 148.9 (s), 138.1 (s), 134.8−137.9 (m), 134.7 (s), 134.1 (s), 132.9−133.1 (m), 132.7 (s), 131.5−131.6 (m), 130.8 (s), 130.5 (s), 125.0 (s), 124.6 (s), 122.9 (s), 122.1 (s), 121.6 (s), 78.3 (d, $^1J_{Rh-C} = 14$ Hz), 76.3 (dd, $^1J_{Rh-C} = 32$ Hz, $^3J_{P-C} = 14$ Hz), 31.3 (s), 30.9 (s); $^{31}P\{^1H\}$ NMR δ 43.8 (d, $^2J_{Rh-P} = 12$ Hz), 27.1 (d, $^2J_{Rh-P} = 3$ Hz). Anal. Calcd for $C_{57}H_{52}P_2N_2Cl_2Rh_2$: C, 62.03; H, 4.75; N, 2.54. Found: C, 61.89; H, 4.55; N, 2.38.

Synthesis of ($N_2C_3H_3$)PPh_2NR, R = Ph (18), 2,6-$Me_2C_6H_3$ (19). These compounds were prepared by similar methods employing the precursor **17**; thus only one representative procedure is described employing the precursor phosphine **17**. To a stirred THF (20 mL) solution of **17** (1.01 g, 4.0 mmol) was added a THF solution of 2,6-$Me_2C_6H_3N_3$ (1.2 g, 8.0 mmol) over 30 min at 25 °C. Gas evolution was observed. The yellow solution was then stirred overnight, and the solvent removed in vacuo. The residue was dissolved in 3−5 mL of THF, and petroleum ether (bp 30−60 °C) was added slowly to precipitate a creamy white solid. The solid was filtered and washed with petroleum ether several times to give a white solid **19**. **18**: Yield 92%; ^1H NMR ($CDCl_3$) δ 7.81−7.93 (m, 4H, PPh_2), 7.39−7.55 (m, 6H, PPh_2), 7.23 (d, $^3J_{H-H} = 2$ Hz, 2H, $N_2C_3H_3$), 6.93−7.02 (m, 2H, NC_6H_5), 6.83 (d, $^3J_{H-H} = 8$ Hz, 2H, NC_6H_5), 6.69 (t, $^3J_{H-H} = 7$ Hz, 1H, NC_6H_5); $^{13}C\{^1H\}$ NMR (THF) (partial) δ 151.4 (s), 139.8 (d, $^1J_{P-C} = 142$ Hz), 132.4 (d,

$^2J_{P-C}$ = 9 Hz), 131.4 (s), 131.1 (s), 128.3 (s), 128.2 (d, $^3J_{P-C}$ = 11 Hz), 125.8 (br), 123.4 (d, $^3J_{P-C}$ = 19 Hz), 116.9 (s); $^{31}P\{^1H\}$ NMR (THF) δ −12.2 (s). Anal. Calcd for $C_{21}H_{18}PN_3$: C, 73.46; H, 5.28; N, 12.24. Found: C, 73.34; H, 5.23; N, 12.45. **19**: Yield 95%; ^1H NMR (d_8-THF) δ 7.83−7.91 (m, 4H, PPh_2), 7.34−7.46 (m, 6H, PPh_2), 7.25−7.26 (m, 2H, $N_2C_3H_3$), 6.78 (d, $^3J_{H-H}$ = 7 Hz, 2H, $Me_2C_6H_3$), 6.42−6.54 (m, 1H, $N_2C_3H_3$), 1.97 (s, 6H, Me); $^{13}C\{^1H\}$ NMR (d_8-THF) δ 144.9, 140.0 (d, $^1J_{P-C}$ = 155 Hz), 132.0 (d, $^3J_{P-C}$ = 89 Hz), 130.0 (d, $^3J_{P-C}$ = 8 Hz), 129.9 (d, $^3J_{P-C}$ = 10 Hz), 129.1, 126.0 (d, $^3J_{P-C}$ = 13 Hz), 125.8 (d, $^3J_{P-C}$ = 3 Hz), 125.6, 122.8, 116.2, 18.5; $^{31}P\{^1H\}$ NMR (d_8-THF) δ −21.4 (s). Anal. Calcd for $C_{23}H_{22}PN_3$: C, 74.38; H, 5.97; N, 11.31. Found: C, 74.24; H, 6.09; N, 11.29.

Generation of [Na(THF)((N$_2$C$_3$H$_2$)PPh$_2$NR)]$_n$, R = Ph (20), 2,6-Me$_2$C$_6$H$_3$ (21). These compounds were prepared by similar methods; thus only one representative procedure is described. To a stirred suspension of NaH (24 mg, 0.96 mmol) in THF (10 mL) was added dropwise a THF solution (10 mL) of **19** (300 mg, 0.810 mmol). Gas evolution occurred immediately, and the suspension was stirred overnight. The solution was filtered through Celite and the solvent removed in vacuo to give a white solid. This was recrystallized with THF/pentane to give colorless crystals of **20**. Yield: 77%; ^1H NMR (d_8-THF) δ 7.91−7.97 (m, 4H, PPh_2), 7.25−7.36 (m, 6H, PPh_2), 7.11−7.16 (m, 2H, $N_2C_3H_2$), 6.80−6.85 (m, 2H, NC_6H_5), 6.71 (d, $^3J_{H-H}$ = 8 Hz, 2H, NC_6H_5), 6.44 (t, $^3J_{H-H}$ = 7 Hz, 1H, NC_6H_5), 3.59−3.64 (m, 4H, THF), 1.74−1.80 (m, 4H, THF); $^{13}C\{H\}$ NMR (d_8-THF) δ 154.2 (s), 143.7 (d, $^1J_{P-C}$ = 185 Hz), 135.6 (d, $^3J_{P-C}$ = 90 Hz), 134.0 (d, $^3J_{P-C}$ = 9 Hz), 133.15 (d, $^3J_{P-C}$ = 9.2 Hz), 131.5 (d, $^3J_{P-C}$ = 16.2 Hz), 132.3 (s), 129.4 (s), 128.4 (d, $^3J_{P-C}$ = 11.2 Hz), 124.4 (d, $^3J_{P-C}$ = 17.7 Hz), 117.3 (s), 68.4 (s), 26.6 (s); $^{31}P\{^1H\}$ NMR (d_8-THF) δ 1.04 (s). **21**: Yield 85%; ^1H NMR (d_8-THF) δ 7.56−7.68 (m, 4H, PPh_2), 7.24−7.26 (m, 2H, $N_2C_3H_2$), 7.15−7.20 (m, 6H, PPh_2), 6.74 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, $Me_2C_6H_3$), 6.45−6.51 (m, 1H, $Me_2C_6H_3$), 3.60−3.61 (m, 4H, THF), 1.93 (s, 6H, Me), 1.75−1.80 (m, 4H, THF); $^{13}C\{H\}$ NMR (d_8-THF) δ 150.5 (s), 144.5 (d, $^1J_{P-C}$ = 187 Hz), 138.0 (d, $^3J_{P-C}$ = 90 Hz), 134.4 (d, $^3J_{P-C}$ = 7.4 Hz), 133.1 (d, $^3J_{P-C}$ = 9 Hz), 131.1 (d, $^3J_{P-C}$ = 17 Hz), 130.6 (s), 128.3 (d, $^3J_{P-C}$ = 2 Hz), 128.1 (d, $^3J_{P-C}$ = 11 Hz), 119.4 (d, $^3J_{P-C}$ = 3 Hz), 117.3 (s), 68.4 (s), 26.6 (s), 21.4 (s); $^{31}P\{^1H\}$ NMR (d_8-THF) δ −4.7 (s).

Synthesis of Rh(COD)((N$_2$C$_3$H$_2$)PPh$_2$NR), R = Ph (22), 2,6-Me$_2$C$_6$H$_3$ (23). These compounds were prepared by similar methods; thus only one representative procedure is described. To a stirred benzene (10 mL) solution of [Rh(μ-Cl)(COD)]$_2$ (67 mg, 0.14 mmol) was added a benzene (5 mL) suspension of **21** (126 mg, 0.28 mmol). The suspension was stirred overnight and filtered through Celite, and the solvent was removed. Recrystallization with benzene/pentane gave a yellow solid. Suitable X-ray quality crystals were grown by slow diffusion of pentane into a concentrated CH_2Cl_2 solution of the compound. **22**: Yield 87%; ^1H NMR (d_8-THF) δ 7.65−7.70 (m, 4H, PPh_2), 7.50−7.53 (m, 2H, PPh_2), 7.37−7.43 (m, 4H, PPh_2), 7.16 (d, $^3J_{H-H}$ = 3 Hz, 1H, $N_2C_3H_2$), 6.98−7.14 (m 2H, NC_6H_5), 6.86−6.92 (m, 1H, NC_6H_5), 6.75−6.80 (m, 3H, NC_6H_5 and $N_2C_3H_2$), 4.21−4.24 (m, 2H, COD), 3.51−3.53 (m, 2H, COD), 2.27−2.47 (m, 4H, COD), 1.82−1.87 (m, 2H, COD), 1.73−1.76 (m, 2H, COD); $^{13}C\{^1H\}$ NMR (d_8-THF) (partial) δ 146.1 (s), 144.6 (d, $^1J_{P-C}$ = 193 Hz), 132.9 (d, $^2J_{P-C}$ = 10 Hz), 132.7 (d, $^3J_{P-C}$ = 15 Hz), 131.9 (s), 129.6 (d, $^3J_{P-C}$ = 6 Hz), 128.1 (d, $^3J_{P-C}$ = 11 Hz), 128.0 (s), 125.5 (d, $^3J_{P-C}$ = 10 Hz), 123.2 (s), 81.8 (d, $^2J_{Rh-C}$ = 12 Hz), 73.2 (d, $^2J_{Rh-C}$ = 13 Hz), 30.6 (s), 30.2 (s); $^{31}P\{^1H\}$ NMR (d_8-THF) δ 24.3 (s). Anal. Calcd for $C_{29}H_{29}N_3PRh$: C, 62.94; H, 5.28; N, 7.59. Found: C, 61.10; H, 5.37; N, 7.10. **23**: Yield 95%; ^1H NMR (d_8-THF) δ 7.66−7.73 (m, 4H, PPh_2), 6.82−7.13 (m, 11H, $N_2C_3H_2$), 4.37−4.39 (m, 2H, COD), 3.25−3.27 (m, 2H, COD), 2.17−2.39 (m, 4H, COD), 2.02 (s, 6H, Me), 1.62−1.74 (m, 2H, COD), 1.51−1.63 (m, 2H, COD); $^{13}C\{H\}$ NMR (d_8-THF) δ 145.0 (d, $^1J_{P-C}$ = 196 Hz), 144.7 (s), 137.5 (d, $^3J_{P-C}$ = 5 Hz), 134.1 (d, $^3J_{P-C}$ = 17 Hz), 133.4 (d, $^3J_{P-C}$ = 10 Hz), 132.9 (s), 130.5 (d, $^3J_{P-C}$ = 132 Hz), 129.4 (s), 129.2 (d, $^3J_{P-C}$ = 12 Hz), 126.7 (d, $^3J_{P-C}$ = 10 Hz), 124.5 (s), 83.7 (d, $^2J_{Rh-C}$ = 12 Hz), 74.5 (d, $^2J_{Rh-C}$ = 14 Hz), 31.7 (s), 31.5 (s), 14.5 (s); $^{31}P\{^1H\}$ NMR (d_8-THF) δ 17.9 (s). Anal. Calcd for $C_{31}H_{33}N_3PRh$: C, 64.03; H, 5.72; N, 7.23. Found: C, 64.43; H, 5.61; N, 7.20.

Computations. All calculations were performed using the Gaussian 98 suite of programs.[33] The structures were optimized with C_s symmetry constraints. Calculations were performed at the DFT level using the hybrid B3LYP method.[34,35] The 6-31G(d) basis set was used on C, H, N, and P. For Ni, the LANL2DZ basis set with corresponding effective core potentials was applied.[36] Natural population analysis[37,38] was performed using the NBO program as implemented by Gaussian 98.

X-ray Data Collection and Reduction. Crystals were manipulated and mounted in capillaries in a glovebox, thus maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5° < 2θ < 45−50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL solution package operating on a Pentium computer.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[39] The heavy atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map

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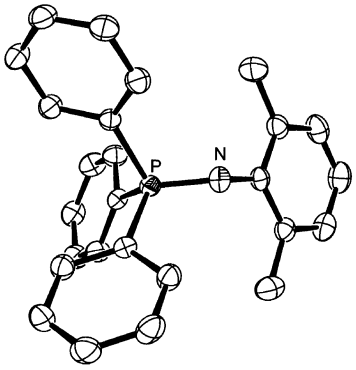


Figure 1. ORTEP drawing of **2** with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond distances and angles: P−N 1.553(2) Å, N−C 1.403(3) Å, P−N−C 132.31(16)°.

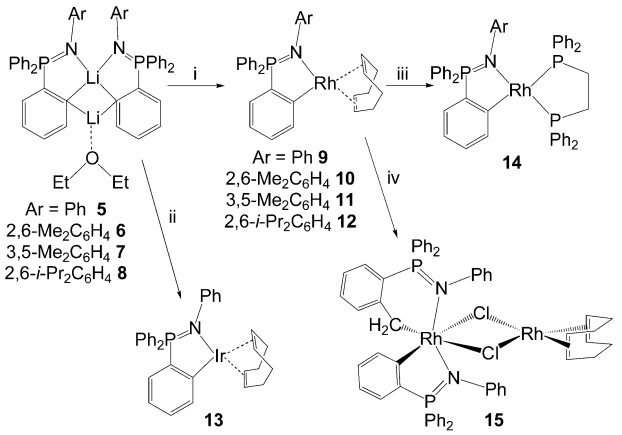
calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Addition details are provided in the Supporting Information.

Results and Discussion

While the phosphinimine Ph_3PNPh is commercially available, the analogues Ph_3PNR (R = 2,6-$Me_2C_6H_3$ **2**, 3,5-$Me_2C_6H_3$ **3**, 2,6-*i*-$Pr_2C_6H_3$ **4**) were synthesized in high yields by oxidation of PPh_3 with the appropriate aryl azide. NMR data were consistent with these formulations and confirmed crystallographically in the case of **2** (Figure 1). The structure is unexceptional with a P−N bond distance of 1.553(2) Å, typical of phosphinimines.[40−42] Subsequent lithiation of these species was performed employing methods similar to those described in the literature for the lithiation of Ph_3PNPh,[31] although the Li reagent and the duration of the reaction were varied with each case. In this way the species of $[Li(o\text{-}C_6H_4PPh_2NPh)]_2\cdot Et_2O$ (R = Ph **5**, 2,6-$Me_2C_6H_3$ **6**, 3,5-$Me_2C_6H_3$ **7**, 2,6-*i*-$Pr_2C_6H_3$ **8**) were obtained in yields ranging from 47 to 85%. NMR data were consistent with lithiation at the *ortho* position of one of the P-bound phenyl rings. The nature of these salts in the solid state is unknown, although it is noteworthy that Steiner et al. have structurally characterized the related Li salt $[Li(o\text{-}C_6H_4PPh_2NSiMe_3)]_2\cdot Et_2O$.[43] Our analogous dimeric formulation is based on NMR and EA data.

Phenylate-Phosphinimine Ligand Complexes. These Li salts react with $[Rh(\mu\text{-}Cl)(COD)]_2$ in THF at room temperature. The resulting complexes Rh(COD)-(o-$C_6H_4PPh_2NR$) (R = Ph **9**, 2,6-$Me_2C_6H_3$ **10**, 3,5-$Me_2C_6H_3$ **11**, 2,6-*i*-$Pr_2C_6H_3$ **12**) were characterized by variety of techniques, including ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, and X-ray diffraction studies (Scheme 1). The chemical shifts of the $^{31}P\{^1H\}$ spectra of these complexes varied with substitution on the N-phenyl ring, resulting in an upfield shift with the presence of electron-donating groups in the 2- and 6-positions. Substitution in the 3- and 5-positions resulted in a $^{31}P\{^1H\}$ resonance very similar to the unsubstituted compound **9**. $^{13}C\{^1H\}$ NMR

Scheme 1



i: $[Rh(\mu\text{-}Cl)(COD)]_2$ ii: $[Ir(\mu\text{-}Cl)(COD)]_2$ iii: $(CH_2PPh_2)_2$ iv: CH_2Cl_2

spectra of these species showed resonances in the range of 170−180 ppm with $^1J_{Rh-C}$ of ca. 40 Hz, consistent with metalation at the *ortho*-aryl carbon. ^1H NMR spectra also showed resonances attributed to two sets of distinct methylene and methine protons of the COD ligand, consistent with the dissymmetry of the metalated phosphinimine ligand. The upfield methylene and methine signals were assigned to those *trans* to the aryl-carbon. This was unambiguously confirmed by a NOESY NMR experiment in the case of **9**. Crystals of **9**−**12** suitable for X-ray structural determination were obtained via recrystallization.

The solid state structures for **9**−**12** were similar (Figure 2). All confirmed the expected pseudo-square-planar coordination sphere about Rh comprised of the σ-bonded aryl carbon, the phosphinimine N donor, and the coordinated COD molecule. The Rh−C and Rh−N distances are similar in these compounds, with the Rh−N distances ranging from 2.105(3)−2.140(2) Å, while the Rh−C distances fall within 2.057(3)−2.071(3) Å, which are only slightly shorter than the Rh−C distance (2.090(1) Å) seen in the Rh(I) species $RhPh(PPh_3)_2(CO)$.[44] Similarly the bite angles of the N−C chelates are similar (**9** 84.90(9)°, **10** 85.08(8)°, **11** 85.06(10)°, **12** 85.54(9)°). The metallocyclic rings are essentially planar and coplanar with the phenyl ring bound to Rh. The N-phenyl ring adopts an orientation that is close to orthogonal to the metallocycle, thereby minimimizing in-plane steric interactions. The N−C distances (1.440(3)−1459(3) Å) are observed to be slightly longer than that seen in the free ligand **2** (1.406(3) Å). Similarly, the P−N bond lengths in the Rh complexes (**9** 1.610(2) Å, **10** 1.613(2) Å, **11** 1.616(3) Å, **12** 1.605(2) Å) were longer than that observed in **2** (1.553(2) Å). These changes in N−C and P−N parameters are consistent with electron donation from N to Rh. The Rh−N−P angles in **9**−**11** were similar at 115.17(12)°, 115.86(10)°, and 115.85(13)°, respectively. In contrast, the corresponding angle in **12** of 112.45(10)° is smaller and may reflect the steric crowding as a result of the presence of the *i*-Pr groups on the N-aryl ring. The Rh−C distances in the Rh(COD) fragments are not equivalent. Those *trans* to the aryl-carbon are

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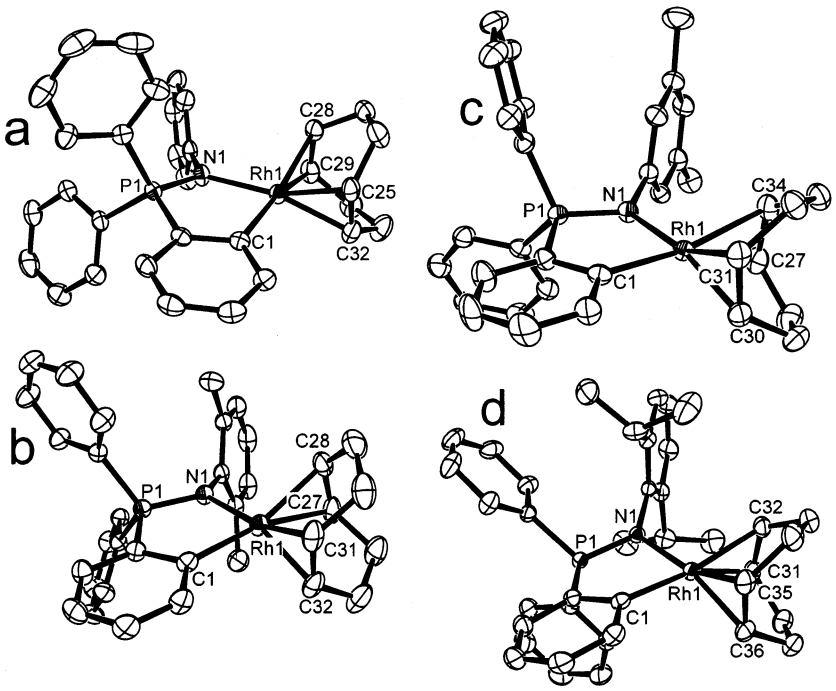

Figure 2. ORTEP drawings of (a) **9**, (b) **10**, (c) **11**, and (d) **12** with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): (a) **9**: Rh(1)−N(1) 2.114(2), Rh(1)−C(1) 2.071(3), P(1)−N(1) 1.610(2), N(1)−C(19) 1.445(3), Rh(1)−C(25) 2.097(3), Rh(1)−C(32) 2.106(3), Rh(1)−C(28) 2.225(3), Rh(1)−C(29) 2.207(3), N(1)−Rh(1)−C(1) 84.90(9), P(1)−N(1)−Rh(1) 115.17(12). For comparison the corresponding data for **13** is provided: Ir(1)−N(1) 2.081(5), Ir(1)−C(1) 2.084(5), Ir(1)−C(25) 2.104(6), Ir(1)−C(26) 2.106(6), Ir(1)−C(30) 2.179(5), Ir(1)−C(29) 2.195(6), P(1)−N(1) 1.628(5), N(1)−C(19) 1.440(7), N(1)−Ir(1)−C(1) 84.77(19), C(19)−N(1)−Ir(1) 126.6(3), P(1)−N(1)−Ir(1) 115.8(3); (b) **10**: Rh(1)−N(1) 2.125(2), Rh(1)−C(1) 2.066(3), P(1)−N(1) 1.613(2), N(1)−C(19) 1.445(3), Rh(1)−C(27) 2.235(3), Rh(1)−C(28) 2.214(3), Rh(1)−C(31) 2.113(3), Rh(1)−C(32) 2.089(3), N(1)−Rh(1)−C(1) 85.08(8), P(1)−N(1)−Rh(1) 115.86(10), C(19)−N(1)−Rh(1) 123.97(16); (c) **11**: Rh(1)−C(1) 2.068(3), Rh(1)−C(31) 2.089(3), Rh(1)−C(30) 2.104(3), Rh(1)−N(1) 2.105(3), Rh(1)−C(27) 2.196(3), Rh(1)−C(34) 2.235(3), P(1)−N(1) 1.616(3), N(1)−C(19) 1.459(4), C(1)−Rh(1)−N(1) 85.06(10), P(1)−N(1)−Rh(1) 115.85(13), C(19)−N(1)−Rh(1) 124.47(19); (d) **12**: Rh(1)−N(1) 2.140(2), Rh(1)−C(1) 2.057(3), P(1)−N(1) 1.605(2), N(1)−C(19) 1.440(3), Rh(1)−C(31) 2.184(3), Rh(1)−C(32) 2.220(3), Rh(1)−C(35) 2.103(3), Rh(1)−C(36) 2.117(3), N(1)−Rh(1)−C(1) 85.54(9), P(1)−N(1)−Rh(1) 112.45(10), C(19)−N(1)−Rh(1) 124.00(15).

longer than those *trans* to the phosphinimine-N. For example, in **9** the Rh(1)−C(28) and Rh(1)−C(29) distances are 2.225(3) and 2.207(3) Å, respectively, whereas the Rh(1)−C(25) and Rh(1)−C(32) distances are 2.097(3) and 2.106(3) Å. Similar differences were also observed in **10**−**12**. These variations are consistent with the greater *trans* influence of the aryl-carbon in comparison to that of N.

In an analogous manner, the Ir analogue of **9**, compound **13**, was prepared using $[Ir(\mu\text{-}Cl)(COD)]_2$ (Scheme 1). NMR data were consistent with the formulation, and X-ray crystallographic data confirmed that **13** was found to be iso-structural to **9**. Ir−C and Ir−N distances were found to be 2.084(5) and 2.081(5) Å. While the Ir−C bond distance is only slightly longer than the corresponding Rh−C distances in **9**, **10**, and **12**, the Ir−N is in fact slightly shorter. Nonetheless, the Ir(COD) fragment exhibits Ir−C distances that follow a pattern similar to those in the Rh complexes, as the Ir−C bonds *trans* to aryl-C are longer (Ir(1)−C(30) 2.179(5) Å; Ir(1)−C(29) 2.195(6) Å) than those *trans* to N (Ir(1)−C(25) 2.104(6) Å; Ir(1)−C(26) 2.106(6) Å). These are similar to those observed in the related Ir complex Ir(COD)((MeC$_6$H$_4$N)PPh$_2$CH(PPh$_2$NC$_6$H$_4$Me).[45]

The reaction of compound **9** with 1.1 equiv of $(CH_2PPh_2)_2$ resulted in replacement of the COD ligand, affording the species Rh(PPh$_2$CH$_2$CH$_2$PPh$_2$)(*o*-C$_6$H$_4$PPh$_2$NPh) (**14**, Scheme 1), as evidenced by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. In particular, the ^{31}P{^{1}H} spectrum showed three distinct signals with the expected Rh−P and P−P couplings. ^{31}P NMR spectroscopy also showed that compound **9** reacted with CH_2Cl_2 to give two products in a ratio of ca. 8:1. The dominant species **15** (Scheme 1) gave rise to two sets of resonances, a doublet centered at 43.7 ppm ($^2J_{Rh-P}$ = 12 Hz) and another doublet centered at 27.1 ppm ($^2J_{Rh-P}$ = 3 Hz), while the minor product **16** afforded a doublet centered at 34.6 ppm ($^2J_{Rh-P}$ = 11 Hz) and a singlet centered at 28.1 ppm. Variable-temperature ^{31}P{^{1}H} NMR spectroscopy showed that the signals broadened slightly upon cooling and the signals from **16** disappeared below −60 °C. This is consistent with an equilibrium between these two species. To characterize the major species, the reaction was repeated with CD_2Cl_2 and monitored by ^{2}D NMR spectroscopy. This experiment revealed the presence of a resonance at 4.2 ppm, which we attribute to a methylene group in the major product.

Although these data suggested oxidative addition of CH_2Cl_2, this was only confirmed by an X-ray study in which the formulation of **15** was confirmed to be [Rh(*o*-C$_6$H$_4$PPh$_2$NPh)(CH$_2$-*o*-C$_6$H$_4$PPh$_2$NPh)(μ-Cl)$_2$Rh(COD)]-

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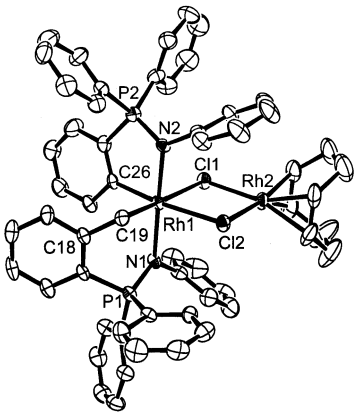
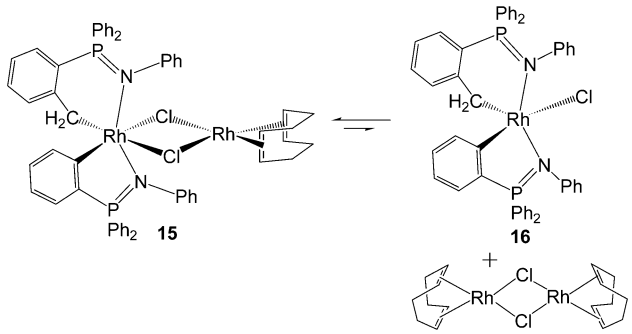


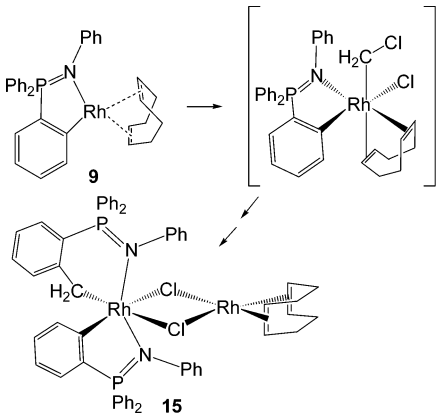
Figure 3. ORTEP drawing of **15** with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−C(26) 2.004(5), Rh(1)−C(19) 2.081(6), Rh(1)−N(2) 2.108(5), Rh(1)−N(1) 2.152(5), Rh(1)−Cl(2) 2.5454(17), Rh(1)−Cl(1) 2.566-(2), Rh(2)−C(54) 2.085(8), Rh(2)−C(57) 2.091(8), Rh(2)−C(53) 2.096(7), Rh(2)−C(50) 2.112(9), Rh(2)−Cl(2) 2.397(2), Rh(2)−Cl(1) 2.4007(18), P(1)−N(1) 1.617(5), P(2)−N(2) 1.603(5), N(1)−C(20) 1.436(8), N(2)−C(44) 1.438(8), C(26)−Rh(1)−C(19) 90.4(2), C(26)−Rh(1)−N(2) 84.4(2), C(19)−Rh(1)−N(2) 88.4(2), C(26)−Rh(1)−N(1) 98.1(2), C(19)−Rh(1)−N(1) 89.7(2), N(2)−Rh(1)−N(1) 176.90(18), C(26)−Rh(1)−Cl(2) 172.91(17), C(19)−Rh(1)−Cl(2) 94.86(17), N(2)−Rh(1)−Cl(2) 90.90(13), N(1)−Rh(1)−Cl(2) 86.78(13), C(26)−Rh(1)−Cl(1) 92.45(16), C(19)−Rh(1)−Cl(1) 174.19(17), N(2)−Rh(1)−Cl(1) 86.78(14), N(1)−Rh(1)−Cl(1) 94.91(14), Cl(2)−Rh(1)−Cl(1) 81.93(5), Cl(2)−Rh(2)−Cl(1) 88.59(6), Rh(2)−Cl(1)−Rh(1) 94.44(6), Rh(2)−Cl(2)−Rh(1) 95.04(6), P(1)−N(1)−Rh(1) 119.2(3), P(2)−N(2)−Rh(1) 116.1(2), P(1)−N(1)−Rh(1) 119.2(3), P(2)−N(2)−Rh(1) 116.1(2).

(**15**). This orange-colored, binucler Rh(I)−Rh(III) complex (Figure 3) consists of a pseudo-octahedral Rh(III) center and a pseudo-square-planar Rh(I) center. These two Rh atoms are bridged by two Cl atoms. The Rh−Cl distances reflect the differing oxidation states. The Rh-(III)−Cl distances average 2.556(2) Å, while the Rh(I)−Cl distances average 2.399(2) Å. The coordination sphere of the Rh(I) is completed by a COD ligand. The Rh−N distances in this fragment are similar to each other and range from 2.085(8) to 2.112(9) Å. One of the original aryl-phosphinimine ligands is bound to the Rh-(III) center; in addition another such ligand has a methylene group inserted into the Rh−C_{aryl} bond. As expected, the Rh−C_{aryl} distance is slightly shorter (2.004(5) Å) than the Rh−CH_2 distance of 2.081(6) Å. This Rh−CH_2 distance is similar to that found in RhI-(C_6H_5)((Ph_2PCH_2)$_2C_6H_3CH_2$) (2.069(4) Å).[46] It is also noteworthy that unlike related Rh(I) species described by Milstein et al., the methylene-arene fragment in **15** shows no evidence of arenium character.[47,48] The C atoms bound to Rh are *cis* (C(26)−Rh(1)−C(19) 90.4-(2)°) and *trans* to the bridging Cl atoms, leaving the two phosphinimine N atoms *trans* to each other with Rh−N distances of 2.108(5) and 2.152(5) Å and a N−Rh−N angle of 176.90(18)°.

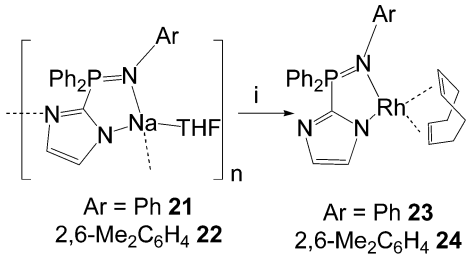
Scheme 2



Scheme 3



Scheme 4



Having unambiguously established the nature of **15**, it was proposed that **16** was a minor product arising from the equilibrium depicted in Scheme 2, although this could not be unequivocally confirmed, as **16** could not be isolated. As for the mechanism of the formation of **15**, this is the subject of speculation (Scheme 3). One is tempted to suggest initial oxidative addition of CH_2Cl_2 to **9** affords a monometallic species containing a RhCl(CH_2Cl) fragment, as has been previous observed in related systems.[1−7] However attempts to spectroscopically observe such an intermediate were not successful. If we speculate that this is the case however, subsequent oxidation addition could afford a bimetallic methylene-bridged species similar to those previously reported.[9,10] Such a complex would then undergo methylene insertion in the Rh−C_{aryl} bond and ligand redistribution to give **15**. Steric congestion could be the driving force for this process. Although similar insertions into Rh−L bonds have been found in other systems,[7,11−13] compound **15** represents the first case where C−C bond formation has resulted.

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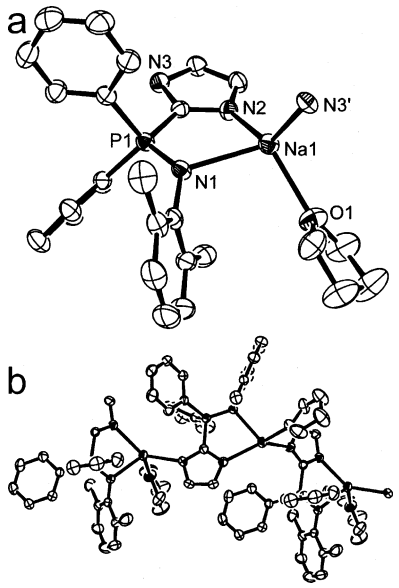

Figure 4. ORTEP drawings of (a) asymmetric unit of **22** and (b) polymeric nature of **22** in solid state with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Na(1)−O(1) 2.363(3), Na(1)−N(2) 2.425(3), Na(1)−N(3) 2.440(3), Na(1)−N(1) 2.460(3), P(1)−N(1) 1.575(2), N(1)−C(13) 1.418(3), N(2)−C(21) 1.352(4), N(2)−C(22) 1.365(4), N(3)−C(21) 1.354(3), N(3)−C(23) 1.361(4), O(1)−Na(1)−N(2) 128.26(10), O(1)−Na(1)−N(3) 97.15(10), N(2)−Na(1)−N(3) 130.60(9), O(1)−Na(1)−N(1) 103.35(10), N(2)−Na(1)−N(1) 77.13(9), N(3)−Na(1)−N(1) 114.07(10), P(1)−N(1)−Na(1) 114.04(12).

Treatment of **10** and **12** with CH_2Cl_2 showed no evidence of reaction even after prolonged stirring. These observations suggested that steric bulk at the 2,6-position of the N-phenyl rings precludes oxidative addition of the CH_2Cl_2 to the Rh center. In contrast, reaction of **11** gave rise to several products with $^{31}P\{^1H\}$ NMR resonances in the range 47−28 ppm. Attempts to separate these products were unsuccessful. It is clear that oxidative addition of CH_2Cl_2 occurs in this case as well, again consistent with the steric arguments.

Imidazolate-Phosphinimine Ligand Complexes. Oxidation of the imidazole-phosphine **17** with organic azides proceeds smoothly to give the corresponding phosphinimines $(N_2C_3H_3)PPh_2NR$, R = Ph **18**, 2,6-$Me_2C_6H_3$ **19**, in high yields (>90%). NMR data confirmed these formulations. These ligands react with NaH at 25 °C in THF to give the corresponding Na-imidazolate-phosphinimines, **20** and **21**, in good yields. NMR spectroscopy was consistent with the formulation of these salts as $[Na(THF)((N_2C_3H_2)PPh_2NR)]_n$, R = Ph **20**, 2,6-$Me_2C_6H_3$ **21**. The nature of **20** was confirmed crystallographically (Figure 4a) to be polymeric in the solid state, in which the imidazolate groups bridge adjacent Na atoms (Figure 4b). The geometry about the Na atom can be described as a distorted tetrahedral coordination sphere of three N atoms and an O atom, allowing for the distortion that results from the presence of the imidazolate-phosphinimine-chelate with the bite angle of 77.13(9)°. The Na−N bond lengths are all similar, falling in the narrow range 2.425(3)−2.460(3) Å.

These salts react with $[Rh(\mu\text{-}Cl)(COD)]_2$ to form the complexes $Rh(COD)((N_2C_3H_2)PPh_2NR)$, R = Ph **22**, 2,6-$Me_2C_6H_3$ **23**, in 95% yields. The ^{31}P NMR spectra of these complexes show the typical downfield shift from the ligand resonance, with the expected Rh−P couplings. Similar to **9**−**13**, NMR spectra for **22** and **23** showed resonances attributable to olefinic and methylene protons of the COD ligand as a result of the asymmetry of the imidazolate-phosphinimine ligand. An X-ray crystallographic study confirmed the structure of **23**, in which cyclooctadiene and a phosphinimine-imidazolate ligand are coordinated to a pseudo-square-planar Rh(I) center. The Rh−imidazolate-N bond distance (2.070(2) Å) is significantly shorter (0.06 Å) than the Rh−phosphinimine-N bond length presumably as a result of the anionic nature of the imidazolate group. It is noteworthy that this Rh−phosphinimine-N distance (2.133(2) Å) is comparable to the $M-C_{aryl}$ distances seen in **9**−**13** as well as to the Rh−N distances reported for $Rh(COD)(CH_2PPh_2(NC_6H_4Me))$ (2.132(3) Å)[49] and $Rh(COD)((MeC_6H_4N)PPh_2CHPPh_2NH(C_6H_4Me))$ (2.144(9) Å).[45] The Rh−imidazolate-N bond length (2.070(3) Å) is slightly longer than the corresponding Rh−pyrrolate-N distance found in $Rh(COD)((NC_5H_4)CH_2NHCH_2(NC_4H_4))$ (2.039(3) Å).[50] Consistent with these differences in the Rh−N distances, the Rh−C bonds reflect the greater *trans* influence of the imidazolate N.

Compounds **22** and **23** did not react with CH_2Cl_2 even after prolonged exposure. While one might invoke a steric argument similar to that used above for **10** and **12** to explain the stability of **23**, the stability of **22** is enigmatic. Clearly the species **22** is sterically similar to **9**, and thus one might have anticipated oxidative addition on that basis. This observation suggests that electronic factors are influencing reactivity in this case. To probe this question, DFT calculations were performed on the ligand−Rh model fragments $[Rh((C_6H_4)PH_2NH)]$ and $[Rh((N_2C_3H_2)PH_2NH)]$. The charge distributions were calculated using both Mulliken atomic charges and natural population analysis (NPA). The calculated charges are tabulated in Table 2. For example, the Mulliken charge on Rh in the phenylate model is 0.004, whereas it is 0.23 in the imidazolate case. The corresponding NPA charges were found to be 0.14 and 0.35, respectively. Although these methods afford differing computed charges, there is consistency in the findingof a higher positive charge on Rh in the imidazolate complex. In addition, the calculated energies of the orbital orthogonal to the Rh−L plane, that is, the pseudo-dz^2 orbital, were found to be −0.16626 and −0.14464 for the imidazole and phenylate models, respectively. These data suggest that weaker donation of electron density from the imidazolate fragment results in a more stable dz^2 orbital on Rh and thus a metal center that is less prone to oxidative addition.

In summary, anionic-phosphinimine ligands based on arylate or imidazolate-phosphinimines have been readily employed to prepare Rh and Ir complexes. In some cases these species undergo oxidative addition of CH_2Cl_2. However, steric congestion above and below the plane

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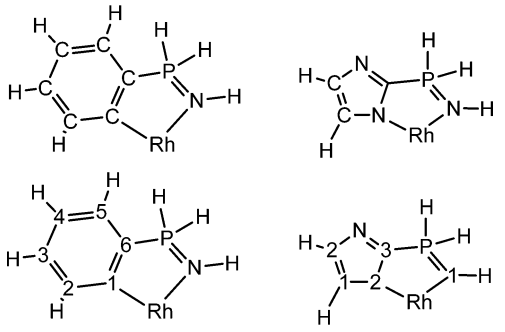
Table 1. Crystallographic Data

	2	**9**	**10**	**11**	**12**
formula	$C_{26}H_{24}NP$	$C_{32}H_{31}NPRh$	$C_{34}H_{35}NPRh$	$C_{38}H_{43}NOPRh$	$C_{38}H_{43}NPRh$
fw	381.43	563.46	591.51	663.61	647.61
a (Å)	9.626(5)	9.835(5)	10.122(6)	21.924(12)	9.927(5)
b (Å)	12.325(7)	11.331(6)	20.056(11)	15.092(8)	11.193(6)
c (Å)	17.721(9)	12.325(7)	14.533(8)	10.022(5)	15.544(8)
		79.137(10)			89.621(10)
β (deg)	92.604(10)	88.477(10)	107.315(11)	95.361(10)	85.158(9)
		77.591(10)			72.044(10)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P\bar{1}$	$P2(1)/n$	$P2(1)/c$	$P\bar{1}$
V (Å^3)	2100.4(19)	1317.3(12)	2817(3)	3301(3)	1636.7(15)
d(calc) (g cm^{-1})	1.206	1.421	1.395	1.335	1.314
Z	4	2	4	4	2
abs coeff, μ (cm^{-1})	0.142	0.730	0.686	0.596	0.597
no. of data collected	8756	5636	11 904	13 754	7043
no. of data $F_o^2 > 3\sigma(F_o^2)$	2334	3736	4018	4690	4655
no. of variables	253	316	334	379	370
R	0.0416	0.0251	0.0231	0.0269	0.0244
R_w	0.1165	0.0683	0.0611	0.0915	0.0630
GOF	1.023	0.982	0.942	0.830	0.929

	13	**15**	**21**	**23**
formula	$C_{32}H_{31}NPIr$	$C_{69}H_{64}Cl_2N_2P_2Rh_2$	$C_{30}H_{35}N_3NaOP$	$C_{31}H_{33}N_3PRh$
fw	652.75	1259.88	500.54	581.48
a (Å)	9.826(5)	10.871(6)	9.167(5)	8.459(5)
b (Å)	11.278(5)	12.726(7)	12.033(6)	9.056(5)
c (Å)	12.306(6)	22.878(12)	25.300(13)	19.201(11)
	79.013(8)	96.295(10)		80.602(12)
β (deg)	88.295(8)	98.239(10)	93.553(9)	78.983(11)
	77.195(9)	99.031(9)		73.660(10)
cryst syst	triclinic	triclinic	monoclinic	triclinic
V (Å^3)	1305.3(11)	3065(3)	2785(2)	1376.0(13)
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
d(calc) (g cm^{-1})	1.661	1.365	1.210	1.403
Z	2	2	4	2
abs coeff, μ (cm^{-1})	5.197	0.720	0.141	0.703
no. of data collected	5508	13 024	11 614	5900
no. of data $F_o^2 > 3\sigma(F_o^2)$	3712	8675	3983	3899
no. of variables	316	694	318	325
R	0.0313	0.0561	0.0459	0.0263
R_w	0.0799	0.1347	0.1274	0.0626
GOF	1.042	1.014	0.979	0.947

Table 2. DFT Computations of Atomic Charge Densities



Rh((C$_6$H$_4$)PH$_2$NH)			Rh((N$_3$C$_3$H$_2$)PH$_2$NH)		
atom	Mulliken charges	NPA charges	atom	Mulliken charges	NPA charges
Rh	0.003533	0.14891	Rh	0.237838	0.35340
P	0.635956	1.38090	P	0.633305	1.35482
N	−0.781775	−1.26335	N(1)	−0.79039	−1.26616
C(1)	0.042648	−0.03488	N(2)	−0.437103	−0.47418
C(2)	−0.190906	−0.2911	C(1)	−0.020848	−0.10116
C(3)	−0.095233	−0.20598	C(2)	−0.045419	−0.09691
C(4)	−0.150775	−0.26783	N(3)	−0.394773	−0.49003
C(5)	−0.113726	−0.20494	C(3)	0.196770	−0.07263
C(6)	−0.166996	−0.50508			

of the Rh(I) coordination sphere provided by ligand substituents inhibits such oxidative addition. Alternatively, oxidation addition is suppressed by electronic perturbations to the ligand which diminish the charge density at Rh. In furthering these studies we are probing the effects of similar ligand perturbations on the reactivity of Rh complexes in catalysis. The results of these efforts will be reported in due course.

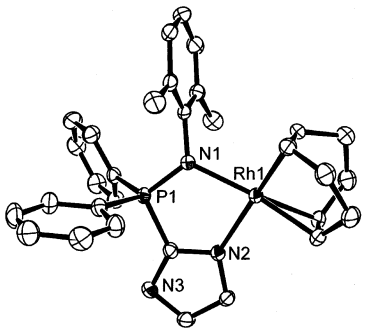


Figure 5. ORTEP drawing of **23** with 30% thermal ellipsoids; hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−N(2) 2.070(2), Rh(1)−C(29) 2.101(3), Rh(1)−C(28) 2.118(3), Rh(1)−N(1) 2.133(2), Rh(1)−C(25) 2.141(3), Rh(1)−C(24) 2.156(3), N(1)−P(1) 1.619(2), N(1)−C(13) 1.455(4), N(1)−P(1) 1.619(2), N(2)−C(21) 1.362(3), N(2)−C(23) 1.369(4), N(3)−C(21) 1.341(4), N(3)−C(22) 1.367(4), N(2)−Rh(1)−N(1) 83.32(9), P(1)−N(1)−Rh(1) 116.57(12).

Acknowledgment. Financial support from NSERC of Canada, NOVA Chemicals Corporation, and the ORDCF is gratefully acknowledged. J.D.M. and J.S.J.Mc. are grateful for the award of an OGS scholarship. D.W.S. is grateful for the award of Forschungpreis from the Alexander von Humboldt Stiftung.

Supporting Information Available: Crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM030539G