Rhodium and Palladium Complexes of a 3,5-Lutidine-Based Phosphine Ligand

Alexander Weisman, Michael Gozin, Heinz-Bernhard Kraatz, and David Milstein*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

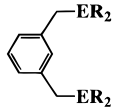
Received August 28, 1995[⊗]

The chelating bis(phosphine) 3,5-bis((diphenylphosphino)methyl)pyridine (dppLH, **9**) was synthesized from 3,5-lutidine by radical chlorination, followed by reaction with $LiPPh_2$. Compound **9** was used to prepare Rh and Pd complexes. The three complexes (dppL)RhL (L = P^iPr_3 (**11**), PPh_3 (**12**), and CO (**13**)) are obtained from $Rh_2Cl_2(COE)_4$ (COE = cyclooctene) and $HRh(PPh_3)_4$. Compound **9** reacts with $(PhCN)_2PdCl_2$ to form the Pd(II) complex (dppL)PdCl (**14**). All complexes are fully characterized. The X-ray crystal structure of **11** has been determined. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with a = 12.242(3) Å, b = 14.384(3) Å, c = 11.653(2) Å, α = 98.61(2)°, β = 96.88(2)°, γ = 106.38(2)°, V = 2023.3(8) Å^3, Z = 2, R = 0.045, and R_w = 0.052. The Rh(I) center is in a square-planar coordination environment with the two phosphines of the dppL ligand framework being *trans* to each other. The pyridine nitrogen is unobstructed and available for binding to other metal centers. Compound **14** acts as a metalloligand toward Pd(II) centers to form the trinuclear complex $\{(dppL)PdCl\}_2PdCl_2$ (**16**). N-coordination of a metal moiety and of a Lewis acid influences the electronic properties on the Pd center.

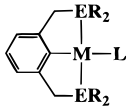
Introduction

Chelating ligand systems based on 1,3-disubstituted benzene (**1**) have been studied extensively over the past years with a variety of donor atoms (E). Particularly fruitful have been studies based on nitrogen,[1] phosphorus,[2] and sulfur[3] as donor atoms. Generally, reactions with suitable metal precursors led to the isolation of orthometallated complexes (**2**) having the two donor atoms of the chelate in a mutual trans arrangement around the metal center. Some of the resulting metal complexes are active as homogeneous catalysts.[4]

This ligand framework offers the possibility for modification at different sites, allowing one to fine tune the electron density



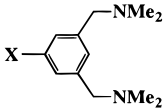
1



2

and possibly to influence the reactivity of a metal center. A change in donor atom (E) and its substituents (R) will influence its binding properties and hence will influence the electron density on the metal center. Whereas the nitrogen-based ligands can be regarded as pure electron donors, phosphorus and sulfur systems are able to interact with a metal center as a donor in a σ/π fashion as well as a π-acceptor due to low-lying σ^*-orbitals.[5] The substituents will have a significant influence on the donor and acceptor behavior of the ligand.

Recently, van Koten et al.[1d] have shown that upon introduction of substituents (X = H, NO_2, NH_2, MeC(O)N(H), Cl, PhCH═N, MeO, MeC(O)) into the *para*-position of the nitrogen-based NCN ligand system (**3**) the electron density on the metal center is influenced through mesomeric or inductive effects.



3

Here, we offer a new approach to influence the electron density on a metal center by having a heteroatom present in

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) (a) Review: van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681. (b) More recent examples: van Koten, G.; Terheijden, J.; van Beek, J. A. M.; Wehman-Ooyevaar, I. C. M.; Müller, F.; Stam, C. H. *Organometallics* **1990**, *9*, 903. (c) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773. (d) van de Kuil, L. A.; Luitges, H.; Grove, D. M.; Zwicker, J. W.; van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468.

(2) (a) Moulton, C. L.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. (b) Rimmel, H.; Venanzi, L. M. *J. Organomet. Chem.* **1983**, *259*, C6. (c) Nemeh, S.; Jernsen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442. (d) Rimmel, H.; Venanzi, L. M. *J. Organomet. Chem.* **1984**, *260*, C52. (e) Rimmel, H.; Venanzi, L. M. *Phosphorous Sulfur Relat. Elem.* **1987**, *30*, 297. (f) Kaska, W. C.; Nemeh, S.; Shirazi, A.; Potuznik, S. *Organometallics* **1988**, *7*, 13. (g) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, *364*, 699. (h) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, *370*, 42. (i) Gorla, F. Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43. (j) Gorla, F.; Togni, A.; Venanzi, L. M.; Albinati, A.; Lianza, F. *Organometallics* **1994**, *13*, 1607. (k) McLoughlin, M. A.; Flesher, R. J.; Kaska, W. C.; Mayer, H. A. *Organometallics* **1994**, *13*, 3816. (l) Kraatz, H.-B.; Milstein, D. *J. Organomet. Chem.* **1995**, *488*, 223. (m) Kennedy, A. R.; Cross, R. J.; Muir, K. W. *Inorg. Chim. Acta* **1995**, *231*, 195. (n) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 9774; *J. Chem. Soc., Chem. Commun.* **1995**, 1965.

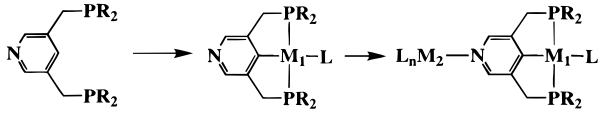
(3) (a) Errington, J.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 2312. (b) Dupont, J.; Beydoun, N.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1989**, 1715.

(4) (a) van Koten; et al. *J. Mol. Catal.* **1988**, *45*, 169. (b) (d^tbppp)PdMe, possessing a metallated aliphatic bisphosphine, was reported to be active toward the amination of activated olefins. Seligson, A. L.; Trogler, W. C. *Organometallics* **1993**, *12*, 744.

(5) (a) Xiao, S.-X.; Trogler, W. C.; Ellis, D. E.; Berkovich-Yellin, Z. B. *J. Am. Chem. Soc.* **1983**, *105*, 7033 (PR_3). (b) Marynick, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 4064 (PR_3). (c) Orpen, A. G.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1310 (PR_3: A crystallographic study on PR_3 transition metal complexes, finding a lengthening of the P−R bond as predicted for an involvement of σ^*-orbitals in back-bonding (see refs 5b,c). (d) Jacobsen, H.; Kraatz, H.-B.; Ziegler, T.; Boorman, P. M. *J. Am. Chem. Soc.* **1992**, *114*, 7851 (a theoretical study on SR_2 binding in face sharing bioctahedral Mo−Mo complexes describing back-bonding to a low-lying σ^*-orbital of thioether). (e) Kraatz, H.-B.; Jacobsen, H.; T. Ziegler, T.; Boorman, P. M. *Organometallics* **1993,** *12*, 76 (a theoretical study on ER_2 (E = O, S, Se) and ER_3 (E = N, P, As) binding (R = H, F, Me) to the $Cr(CO)_5$ fragment; quantifying σ-donation and π-back-bonding).

0020-1669/96/1335-1792$12.00/0 © 1996 American Chemical Society

the *trans*-position of the aromatic ring of a terdentate chelating bis(phosphine) ligand. Our ligand will be based on a 3,5-lutidine backbone, possessing pending methylene−phosphino groups in the 3,5-positions (**4**). Reaction of the ligand with a suitable



metal precursor should lead to complex **5**, leaving the nitrogen-donor atom in the heteroaromatic ring available for binding to another metal moiety. Coordination of this metalloligand through the heteroatom to a second metal center (L_nM_2), giving **6**, should directly influence the electronic properties of on M_1. Coordination of different metal fragments to the metalloligand may allow us to influence the electronic properties of M_1 over a wide range.

Using appropriate spectroscopic techniques, it should be possible to monitor metal binding to the pyridine nitrogen and to evaluate electronic influences on M_1. In this paper, we are detailing our synthetic approaches to the ligand and our results on metal binding studies, some of which have been communicated before.[6]

Experimental Section

General. Materials. All reactions were carried out under nitrogen atmosphere in a Vacuum Atmospheres glovebox (DC-882) equipped with a recirculation (MO-40) "Dri Train" or under argon using standard Schlenk techniques. All solvents were rigorously dried by reflux over the appropriate drying agents and degassed prior to storage in the glovebox over 4 Å molecular sieves: CCl_4 (Frutarom), benzene (Frutarom, sodium−benzophenone), toluene (Frutarom, sodium−benzophenone), pentane (Merck, sodium−benzophenone, tetraglyme), tetrahydrofuran (Biolab, sodium−benzophenone), and dichloromethane (Frutarom, P_2O_5). All deuterated solvents were purchased from Aldrich, degassed, and stored over 4 Å molecular sieves in the glovebox. P^iPr_3 (Strem), NEt_3 (Aldrich), 3,5-lutidine (Aldrich), BEt_3 (1 M in hexanes, Aldrich), and *N*-chlorosuccinimide (Fluka) were used as received. $LiPPh_2$,[7] $Rh_2Cl_2(COE)_4$ (COE = cyclooctene),[8] $HRh(PPh_3)_4$,[9] and $(PhCN)_2PdCl_2$[10] were prepared according to the literature procedures.

Spectroscopy. ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 400.19, 128.4, 161.9, and 100.6 MHz, respectively, using a Bruker AMX 400 NMR spectrometer. ^{1}H NMR spectra are referenced to the residual proton resonance of the solvents. ^{11}B NMR spectra are referenced to external $BF_3{\cdot}OEt_2$. ^{31}P NMR spectra are referenced to external 85% H_3PO_4 (in D_2O). IR spectra were recorded as films between NaCl plates on a Nicolet 510 FT spectrometer.

Synthesis of dppLH: (a) 3,5-Bis(chloromethyl)pyridine (8). A refluxing solution of 3,5-lutidine (20.0 g, 0.187 mol) and *N*-chlorosuccinimide (40.0 g, 0.300 mol) in CCl_4 (2.5 L) was irradiated for 16 h with a Hg lamp. The progress of the chlorination of the methyl groups was monitored by GC. After the concentration of 3,5-bis(chloromethyl)pyridine in the reaction mixture had reached 65−70% (based on 3,5-lutidine), irradiation was stopped and the solution allowed to cool to room temperature. The reaction mixture was filtered, and dry HCl gas was bubbled through the solution for 20 min. The yellow-white precipitate containing the desired 3,5-bis(chloromethyl)pyridine hydrochloride was filtered off, dried, and recrystallized from ^{i}PrOH at 0 °C. After the product was redissolved in water and solution was filtered, its pH was adjusted to pH 8 by the addition of a saturated aqueous solution of Na_2CO_3. The yellow-brown precipitate which formed was collected by filtration, washed with water (3 × 50 mL) and cold pentane (3 × 15 mL), and then dried. The crude product was recrystallized from hexane to give 3,5-bis(chloromethyl)pyridine in low yield (1.5 g, 4.6%), mp 86−87 °C. ^{1}H NMR (C_6D_6): δ 8.2 (2H, d, $^4J_{HH}$ = 2.2 Hz, H_o), 6.8 (1H, m, $^4J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 0.4 Hz, H_p), 3.7 (4H, d, $^4J_{HH}$ = 2.2 Hz, $-CH_2Cl$). ^{13}C{^{1}H} NMR (C_6D_6): δ 149.6 (s, HC_o), 135.8 (s, HC_p), 133.2 (s, HC_m), 42.6 (s, CH_2Cl). This compound is unstable due to pyridine quaternization and should be stored at −30 °C.

(b) 3,5-Bis((diphenylphosphino)methyl)pyridine (dppLH, 9). 3,5-Bis(chloromethyl)pyridine (3 g, 16.8 mmol) was added dropwise to a red solution of $LiPPh_2$ (6.5 g, 33.9 mmol) in THF (50 mL) at −78 °C. After the addition was complete, the solution was allowed to warm up to room temperature and the solvent was removed in vacuo. The resulting residue was extracted with toluene (3 × 50 mL). The combined extracts were reduced in vacuo to a volume of 10 mL and then chromatographed on a silica column (60−230 mesh, Merck). Gradient elution from pure CH_2Cl_2 to a 1:1 mixture of CH_2Cl_2:THF was used to achieve maximum separation. The fractions containing the desired compound were pumped to dryness. The resulting air-sensitive colorless oil was recrystallized from pentane, yielding 3,5-bis((diphenylphosphino)methyl)pyridine as a colorless solid (2.8 g, 35%). Anal. Calcd for $C_{31}H_{27}NP_2$: C, 78.30; H, 5.72; N, 2.95. Found: C, 78.54; H, 5.70; N, 2.55. ^{31}P{^{1}H} NMR ($CDCl_3$): δ −10.22 (s). ^{1}H NMR ($CDCl_3$): δ 7.92 (2H, br s, H_o of NC_5H_3), 7.20 (20H, m, H of PC_6H_5), 7.13 (1H, s, H_p of NC_5H_3), 3.25 (4H, s, CH_2P). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 147.91 (br m, C_o of NC_5H_3), 137.42 (d, $^1J_{CP}$ = 18.1 Hz, C_i of PC_6H_5), 132.83 (d, $^2J_{CP}$ = 18.6 Hz, C_o of PC_6H_5), 132.6 (br t, $^3J_{CP}$ = 7.7 Hz, C_p of NC_5H_3), 131.0 (br m, C_m of NC_5H_3), 128.96 (s, C_p of PC_6H_5), 128.49 (d, $^3J_{CP}$ = 6.7 Hz, C_m of PC_6H_5), 36.50 (d, $^1J_{PC}$ = 15.9 Hz, CH_2P).

Synthesis of (dppL)RhP^{i}Pr$_3$ (11). To a stirring solution of $Rh_2Cl_2(COE)_4$ (40 mg, 0.056 mmol) in THF (30 mL), a solution of dppLH (53 mg, 0.112 mmol) and P^iPr_3 (180 mg, 112.5 mmol) in THF/NEt_3 (1:1; 30 mL) was added. The turbid brown reaction mixture was stirred at room temperature for 12 h, and then all volatiles were stripped off. To the remaining oily brown residue, benzene (5 mL) was added. The benzene solution was filtered through a cotton pad and then pumped to dryness. A ^{31}P{^{1}H} NMR spectrum of an aliquot indicated the presence of the desired Rh(I) complex. After extraction of the residue with pentane (5 × 5 mL), the combined extracts were pumped to dryness, yielding 11 mg of the desired (dppL)RhP^{i}Pr$_3$ as an orange crystalline solid. ^{31}P{^{1}H} NMR (C_6D_6): δ 51.31 (dd, $^1J_{PRh}$ = 165 Hz, $^2J_{PP}$ = 29 Hz, 2P of dppL), 47.80 (dt, $^1J_{PRh}$ = 116 Hz, $^2J_{PP}$ = 29 Hz, 1P of PPh_3). ^{1}H NMR (C_6D_6): δ 6.8−8.4 (m, 22H, *aromatics*), 3.72 (br s, 4H, CH_2P), 1.69 (sepd, $^2J_{HP}$ = 2.3 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, $P(CH(CH_3)_2$; collapsing into a septet upon ^{31}P decoupling $^3J_{HH}$ = 7.1 Hz), 1.06 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{HP}$ = 11.7 Hz).

Synthesis of (dppL)RhPPh$_3$ (12). To a suspension of $HRh(PPh_3)_4$ (400 mg, 0.347 mmol) in THF (60 mL), a solution of dppLH (165 mg, 0.347 mmol) in THF (10 mL) was added. The reaction was stirred for 12 h and then reduced in vacuo to a volume of ca. 2 mL. Addition of 15 mL cold pentane induced precipitation of an orange solid, which was collected and then dried in vacuo, giving 212 mg of the desired product (yield: 73%). ^{31}P{^{1}H} NMR (C_6D_6): δ 52.1 (dd, $^1J_{PRh}$ = 161 Hz, $^2J_{PP}$ = 30 Hz, 2P of dppL), 37.3 (dt, $^1J_{PRh}$ = 120 Hz, $^2J_{PP}$ = 30 Hz, 1P of PPh_3). ^{1}H NMR (C_6D_6): δ 8.52 (2H, br s, H_m of NC_5H_3), 6.7−7.6 (35H, m, *aromatics*), 3.71 (4H, vt, $^2J_{HP}$ = 3.6 Hz, CH_2P). ^{13}C{^{1}H} NMR (C_6D_6): δ 188.5 (m, C_i of NC_5H_3), 144.1 (dvt, $^2J_{CP}$ = 13 Hz, $^2J_{CRh}$ = 1 Hz, C_o of NC_5H_3), 141.1 (dvt, $^2J_{CP}$ = 9 Hz, $^2J_{CP}$ = 2 Hz, C_m of NC_5H_3), 138.7 (dt, $^1J_{CP}$ = 31 Hz, $^3J_{CP}$ = 2 Hz, C_i of PPh_3), 137.3 (td, $^3J_{CP}$ = 17 Hz, $^1J_{CP}$ = 2 Hz, C_i of PC_6H_5), 134.6 (d, $^2J_{CP}$ = 13 Hz, Ph), 133.6 (dt, $^2J_{CP}$ = 6 Hz, J_{CP} = 2 Hz, Ph), 128.9 (t, J_{CP} = 4 Hz, Ph), 128.6 (d, $^4J_{CP}$ = 1 Hz, Ph), 127.5 (d, $^3J_{CP}$ = 9 Hz, Ph), 46.8 (ddvt, $^1J_{CP}$ = 14 Hz, $^3J_{CP}$ = 8 Hz, J = 2.6 Hz, CH_2P).

Synthesis of (dppL)RhCO (13). A Fischer−Porter flask was charged with a suspension of (dppL)$RhPPh_3$ (50 mg, 0.060 mmol) in 20 mL of pentane and then pressurized with 20 psi of CO. The reaction mixture was stirred for 12 h. The desired product precipitated from solution as a yellow solid. The solid was washed with two portions of

(6) Gozin, M.; Weisman, A.; Milstein, D. Abstract presented at the XVth International Conference on Organometallics Chemistry, Warsaw, August 9−14, 1992; Abstract O23.
(7) Luther, G. W., III; Beyerle, G. *Inorg. Synth.* **1977**, *17*, 186.
(8) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 92.
(9) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 843.
(10) (a) Kharash, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882−884. (b) Dietl, H.; Reinheimer, H.; Moffat, J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2276−2285.

Table 1. Crystallographic Data for (dppL)Rh(P^iPr_3)·C_6H_6 (**11**·C_6H_6)

formula	$C_{46}H_{53}NP_3Rh$	V, Å^3	2023.3 (8)
fw	801.8	Z	2
space group	$P\bar{1}$ (No. 2)	ρ_{calc}, g/cm^{-3}	1.387
a, Å	12.242 (3)	cryst size, mm	0.4 × 0.4 × 0.3
b, Å	14.384 (3)	μ (Mo Kα), cm^{-1}	5.64
c, Å	11.653 (2)	radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å; graphite monochromated)
α, deg	98.61 (2)	R^a	0.045
β, deg	96.88 (2)	$R_w{}^{b,c}$	0.052
γ, deg	106.38 (2)		

[a] $R = \sum\Delta F/\sum|F_o|$. [b] $R_w = \sum w^{1/2}(\Delta F)/\sum w^{1/2}F_o$. [c] Weights are defined as $w = 1.1754/[\sigma^2(F) + 0.000126F^2]$.

pentane (2 × 10 mL) and dried in vacuo (34 mg, 95% yield). $^{31}P\{^1H\}$ NMR: C_6D_6, δ 58.0 (d, $^1J_{PRh}$ = 155 Hz); in THF-d_8, δ 57.8 (d, $^1J_{PRh}$ = 155 Hz); in acetone-d_6, δ 58.7 (d, $^1J_{PRh}$ = 155 Hz). ^1H NMR: in C_6D_6, δ 7.80 (2H, bs, H_m of NC_5H_3), 6.4−7.2 (20H, m, all H of PC_6H_5), 2.80 (4H, bs, CH_2P); in THF-d_8, δ 7.79 (2H, bs, H_m of NC_5H_3), 6.8−7.5 (20H, m, all H of PC_6H_5), 3.29 (4H, bs, CH_2P); in acetone-d_6, δ 7.83 (2H, bs, H_m of NC_5H_3), 7.1−7.5 (20H, m, all H of PC_6H_5), 3.34 (4H, bs, CH_2P). $^{13}C\{^1H\}$ NMR in C_6D_6 (carbons of *C*O and C_{ipso} were not observed), δ 143.3 (vt, $^2J_{CP}$ = 13 Hz, C_o of NC_5H_3), 142.1 (vt, $^2J_{CP}$ = 9 Hz, C_m of NC_5H_3), 139.6 (t, J = 14 Hz), 133.3 (bs), 132.4 (d, J = 10 Hz), 132.1 (t, J = 6 Hz), 131.5 (d, J = 3 Hz), 131.3 (d, J = 9 Hz), 128.6 (vt, J = 4 Hz), 42.4 (vt, $^1J_{CP}$ = 15 Hz, *C*H$_2$P); in THF-d_8, δ 206.0 (m, Rh*C*O), 185.7 (m, C_i of NC_5H_3), 143.3 (vt, $^2J_{CP}$ = 13 Hz, C_o of NC_5H_3), 143.3 (m), 140.2 (t, J = 14 Hz), 138.5 (bs), 133.8 (bs), 132.8 (d, J = 10 Hz), 132.5 (t, J = 6 Hz), 125.9 (s), 42.3 (vt, $^1J_{CP}$ = 15 Hz, *C*H$_2$P). IR (ν in cm^{-1}, NaCl, film): 1955 (ν_{CO}).

Synthesis of (dppL)PdCl (14). To a vigorously stirred solution of $(PhCN)_2PdCl_2$ (100 mg, 0.26 mmol) in CH_2Cl_2 (20 mL) in a pressure vessel, a solution of dppLH (124 mg, 0.26 mmol) in CH_2Cl_2 (30 mL) was slowly added. Immediately the color of the solution changed from orange-red to bright yellow, and a small amount of a yellow precipitate appeared. The pressure vessel was heated to 100 °C for 12 h, after which a bright yellow suspension had formed. The reaction mixture was pumped to dryness, yielding the pyridinium hydrochloride as a yellow solid ([(dppLH)PdCl]$^+$Cl$^-$: Anal. Calcd for $C_{31}H_{27}Cl_2NP_2Pd$·$2CH_2Cl_2$: C, 48.18; H, 3.80; N, 1.70. Found: C, 48.24; H, 4.02; N, 1.83.). It has the following spectroscopic properties ($^{31}P\{^1H\}$ NMR: in DMSO-d_6, δ 40.27 (s); in CH_3OD, δ 39.70 (s). ^1H NMR (DMSO-d_6): δ 8.45 (2H, s, H_m of NC_5H_3), 7.91 (8H, m, H_o of PC_6H_5), 7.54 (12H, m, H_m and H_p of PC_6H_5), 4.42 (4H, vt, $^2J_{HP}$ = 4.74Hz, CH_2P). vis (λ in nm (ϵ in L mol^{-1}cm^{-1}): 406 (322)). In order to obtain the free base, the hydrochloride was treated with a mixture of toluene (40 mL), Et_3N (5 mL), and water (20 mL) and the organic phase was collected. The remaining aqueous phase was extracted twice with toluene (2 × 20 mL), the combined organic phases pumped to dryness, and the remaining orange solid recrystallized from benzene, giving 101 mg of orange crystals (0.164 mmol; 63%). $^{31}P\{^1H\}$ NMR: in $CDCl_3$, δ 33.07 (s); in C_6D_6, δ 36.50 (s); in acetone-d_6, δ 41.30 (s). ^1H NMR ($CDCl_3$): δ 8.21 (2H, s, H_m of NC_5H_3), 7.81 (8H, m, H_o of PC_6H_5), 7.36 (12H, m, H_m and H_p of PC_6H_5), 3.90 (4H, vt, $^2J_{HP}$ = 4.7 Hz, CH_2P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.89 (s, C_i of NC_5H_3), 144.81 (vt, $^2J_{CP}$ = 11 Hz, C_o of NC_5H_3), 143.73 (vt, $^2J_{CP}$ = 11 Hz, C_m of NC_5H_3), 133.56 (vt, $^2J_{CP}$ = 6.7 Hz, C_o of PC_6H_5), 131.92 (vt, $^1J_{CP}$ = 21.7 HzC_i of PC_6H_5), 131.55 (s, C_p of PC_6H_5), 129.56 (vt, $^2J_{CP}$ = 5 Hz, C_m of PC_6H_5), 46.8 (vt, $^1J_{CP}$ = 15 Hz, *C*H$_2$P). vis (λ in nm (ϵ in L mol^{-1}cm^{-1}): 422 (245). FD MS: *m/e* 607.

Synthesis of {(dppL)PdCl}·BEt_3 (15). BEt_3 (35 μL; 1 M solution in hexanes) was added to a stirring solution of (dppL)PdCl (20 mg, 0.032 mmol) in benzene (2 mL). After 2 h all volatiles were removed in vacuo. The remaining orange solid was washed with pentane (3 × 5 mL) and then dried in vacuo. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.55 (s). ^1H NMR ($CDCl_3$): δ 8.19 (2H, s, H_m of NC_5H_3), 7.86 (8H, m, H_o of PC_6H_5), 7.46 (12H, m, H_m and H_p of PC_6H_5), 4.01 (4H, s br, CH_2P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 177.90 (s br, C_i of NC_5H_3), 146.88 (vt, $^2J_{CP}$ = 11.9 Hz, C_o of NC_5H_3), 138.47 (vt, $^2J_{CP}$ = 10.5 Hz, C_m of NC_5H_3), 133.78 (vt, $^2J_{CP}$ = 6.8 Hz, C_o of PC_6H_5), 132.06 (vt, $^1J_{CP}$ = 22.0 Hz, PC_6H_5), 131.77 (s, C_p of PC_6H_5), 129.73 (vt, $^2J_{CP}$ = 5.2 Hz, C_m of PC_6H_5), 40.06 (vt, $^1J_{CP}$ = 15.0 Hz, *C*H$_2$P), 16.87 (s br, B*C*H$_2$-CH$_3$), 11.25 (s, BCH$_2$*C*H$_3$). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 1.5. vis (λ in nm (ϵ in L mol^{-1}cm^{-1}): 420 (276).

Synthesis of {(dppL)PdCl}$_2$$PdCl_2$ (16). A solution of $(PhCN)_2PdCl_2$ (8 mg, 0.021 mmol) in THF (5 mL) was added dropwise to a stirring solution of (dppL)PdCl (27 mg, 0.044 mmol) in THF (10 mL). The reaction mixture was stirred for 12 h, then pumped to dryness, and then redissolved in $CDCl_3$ for NMR measurements. The product was obtained in a crystalline form from the NMR solvent. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.74 (s). ^1H NMR ($CDCl_3$): δ 8.38 (2H, s, H_m of NC_5H_3), 7.82 (8H, m, H_o of PC_6H_5), 7.45 (12H, m, H_m and H_p of PC_6H_5), 3.96 (4H, vt, $^2J_{HP}$ = 4.6 Hz, CH_2P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.89 (s, C_i of NC_5H_3), 146.25 (vt, $^2J_{CP}$ = 11.8 Hz, C_o of NC_5H_3), 146.03 (vt, $^2J_{CP}$ = 11.4 Hz, C_m of NC_5H_3), 133.46 (vt, $^2J_{CP}$ = 6.9 Hz, C_o of PC_6H_5), 131.85 (s, C_p of PC_6H_5), 130.96 (vt, $^1J_{CP}$ = 22.4 HzC_i of PC_6H_5), 129.73 (vt, $^2J_{CP}$ = 5.3 Hz, C_m of PC_6H_5), 40.34 (vt, $^1J_{CP}$ = 14.8 Hz, *C*H$_2$P). vis (λ in nm (ϵ in L mol^{-1}cm^{-1}): 420 (305). FAB MS: *m/e* 1406.2 [M$^+$].

X-ray Crystal Structure Analysis of (dppL)Rh(P^iPr_3)·C_6H_6. Pertinent crystallographic information is summarized in Table 1. Crystals of crystallographic quality were obtained from benzene. An orange prism of appropriate size (0.4 × 0.4 × 0.3 mm) was selected and mounted on a glass fiber using silicone grease and placed on a Rigaku AFC5R diffractometer equipped with a rotating anode (RU-300). Data collection proceeded at 90 K. The unit cell was obtained by a random search of 20 carefully centered reflections. Monitoring of three standard reflections every 200 reflections indicated no decay of the crystal in the X-ray beam. Data were collected at constant scan speed (8°/min) in the Ω-scan mode in the range of $2° < 2\theta < 55°$, giving a total of 9817 relections (7776 with $I > 3\sigma(I)$). The data were corrected for Lorentz and polarization effects. No absorption correction was applied to the data due to the low absorption coefficient (μ = 5.64 cm^{-1}). The structure was solved by automated Patterson analysis (SHELXS-86)[11] and Fourier methods (SHELX-76).[12] Hydrogen atoms were found from the difference Fourier map and refined with an overall temperature factor ($U_{overall}$ = 0.044(2) × 10^3 Å^2). Scattering factors and corrections for anomalous dispersion for Rh and P were those of the *International Tables for Crystallography*.[13]

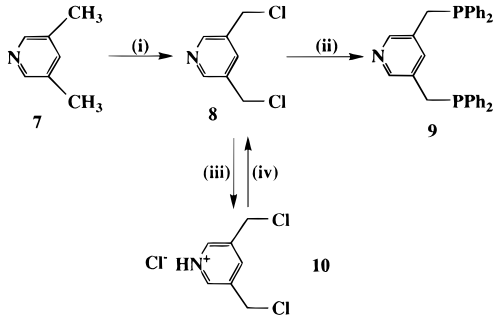
Results and Discussion

(a) Ligand Synthesis. The synthetic route for the preparation of **9** is summarized in Scheme 1. 3,5-Bis(chloromethyl)pyridine (**8**) was obtained in low yield by radical chlorination of 3,5-lutidine (**7**) with *N*-chlorosuccinimide in refluxing CCl_4.

The chlorination was nonselective, leading to a mixture of products, containing mainly the desired **8**. To prevent polymerization of the free base by quaternization of the pyridine moiety, **8** was converted to its hydrochloride **10**. We found that the free base polymerized upon standing for a few days, even at −10 °C.[14] Therefore, the free base had to be prepared freshly from **10** by deprotonation with $NaHCO_3$ in water at pH 8. Compound **8** reacted with $LiPPh_2$ in THF at −78 °C to give **3** as a colorless solid in moderate yields.

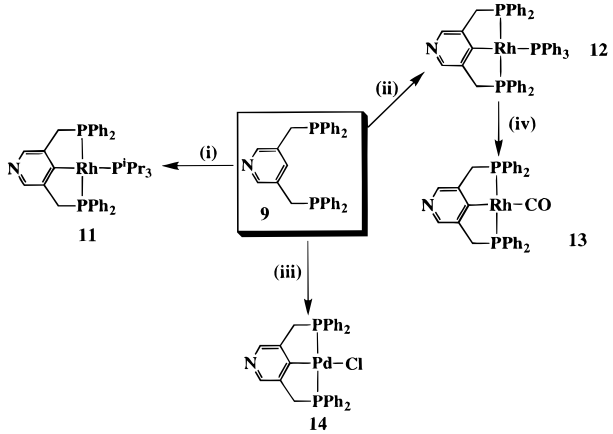
(11) Sheldrick, G. M. SHELXS86, University of Gottingen, F.R.G., 1986.
(12) Sheldrick, G. M. SHELX76, Cambridge University, England, 1976.
(13) *International Tables for Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4.
(14) Similar attempts using radical bromination with *N*-bromosuccinimide and other bromination reagents (Br_2PPh_3, Br_2, and poly(vinylpyridinium hydrotribromide)) led to formation of polymeric products by N-alkylation of the desired 3,5-bis(bromomethylene)pyridine.

Scheme 1. Synthesis of dppLH: (i) *N*-Chlorosuccinimide, CCl_4, Reflux, *hν*; (ii) $LiPPh_2$, THF, −78 °C; (iii) HCl_{gas}, CCl_4; (iv) $NaHCO_3$, H_2O, pH 8



(b) Syntheses of Metal Complexes. Compound **9** forms stable complexes with a variety of metals. Our synthetic approaches are summarized in Scheme 2.

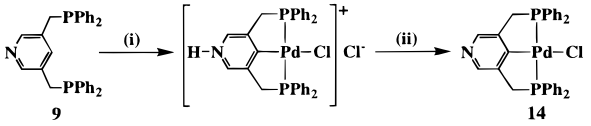
Scheme 2. Syntheses of (dppL)Rh Complexes: (i) $Rh_2Cl_2(COE)_4$, P^iPr_3, THF/NEt_3 (3:1), 12 h, RT; (ii) $HRh(PPh_3)_4$, THF, 12 h, RT; (iii) $(PhCN)_2PdCl_2$, CH_2Cl_2; Toluene/Water/NEt_3 (10:2:1), Reflux; (iv) CO (20 psi), Pentane, 12 h, RT



The reaction of **9** with $Rh_2Cl_2(COE)_4$ and P^iPr_3 in THF/NEt_3 (3:1) leads to the formation of the mononuclear Rh(I) complex **11**, which is obtained as a crystalline yellow material from benzene. Absence of base results in the formation of an intractable viscous solid. As expected, **11** exhibits two signals in the $^{31}P\{^1H\}$ NMR spectrum (intensity ratio of 2:1) in accord with the X-ray structure determination (*vide infra*). The signal at δ 51.31, exhibiting a doublet of doublets splitting pattern ($^1J_{PRh}$ = 165 Hz, $^2J_{PP}$ = 29 Hz), is assigned to the two phosphorous nuclei of the dppL framework. The second signal is observed at δ 47.80 and is assigned to the unique phosphorous of the P^iPr_3 ligand, being *trans* to the aromatic ring. Coupling to the ^{31}P nuclei of the two phosphines of the dppL ligand and to ^{103}Rh gives rise to a doublet of triplets ($^1J_{PRh}$ = 116 Hz, $^2J_{PP}$ = 29 Hz). In the ^1H NMR spectrum the methylene protons of the $-CH_2P$ group are observed as a broad singlet at δ 3.72. All ^{i}Pr groups of the P^iPr_3 are magnetically identical, giving rise to one doublet of septets for the methine proton at δ 1.69 and a doublet of doublets for the methyl protons at δ 1.06.

The analogous PPh_3 complex **12** can be obtained conveniently from $HRh(PPh_3)_4$ and **9** in THF. Its spectroscopic properties are similar to those of **11**. It exhibits two signals in the ^{31}P NMR in an intensity ratio of 2:1. The signal at δ 52.10 (doublet of doublets, $^1J_{PRh}$ = 161 Hz, $^2J_{PP}$ = 30 Hz) is assigned to the two phosphine substituents of the dppL ligand. The second signal is observed at δ 37.3 (doublet of triplet, $^1J_{PRh}$ =120 Hz, $^2J_{PP}$ = 30 Hz). Multiplicities and coupling constants are comparable to those of **11**. The orthometallated carbon atom is observed as a multiplet at δ 188.5 in the $^{13}C\{H\}$ NMR spectrum. The methylene protons of the $-CH_2P$ group are observed as a virtual triplet at δ 3.71. The synthetic approach starting from $HRh(PPh_3)_4$ has the disadvantage of 3 equiv of PPh_3 being produced en route to **12**, which are extremely difficult to remove since both have very similar solubility properties. However, this has no effect on the further chemistry of complex **12**.

Scheme 3. Synthesis of (dppx)PdCl (**14**): (i) $(PhCN)_2PdCl_2$ in CH_2Cl_2; (ii) Et_3N, Toluene, Water



The reaction pathway to **11** most likely involves substitution of the olefin by the bis(phosphine) followed by oxidative metallation of the heteroaromatic ring to give a Rh(III) species. This will then reductively eliminate HCl to give the Rh(I) complex **11**. NEt_3 will remove HCl from the solution and form $[HNEt_3]^+Cl^-$. Bases have been used before to abstract HCl from Rh(III) hydrido chlorides.[2c] In the absence of added base, two possible competing reactions may occur, involving formation of the pyridinium hydrochloride salt and formation of a Rh(III) hydrido chloride complex. For the formation of **12** a similar reaction sequence in envisioned, involving coordination of the bis(phosphine), followed by orthometallation to give a Rh(III) bishydrido complex, which readily eliminates dihydrogen to give **12**.

The PPh_3 ligand in **12** *trans* to the aromatic ring is labile and can be substituted by CO. Pressurizing a solution of **12** in pentane with 20 psi of CO leads to the quantitative precipitation of the yellow RhCO complex **13**. Excess phosphine can now be conveniently removed by washing the yellow solid with pentane. Complex **13** exhibits a single doublet in the ^{31}P NMR spectrum at significantly lower field as compared to **11** and **12** at δ 58.00 ($^1J_{PRh}$ = 155 Hz). The shift of $-CH_2P$ in the ^1H NMR is extremely solvent dependent (in C_6D_6, δ 2.80; in THF-d_8, δ 3.29; in acetone-d_6, δ 3.34). The complex exhibits a single ν_{CO} at 1955 cm^{-1}, indicating significant back-bonding to the CO ligand in accord with the observed downfield shift in the ^{31}P NMR spectrum.

During the reaction of $(PhCN)_2PdCl_2$ with **9** in CH_2Cl_2 1 equiv of HCl is produced, which is trapped by the basic nitrogen, leading to the formation of the hydrochloride $[(HdppL)PdCl]^+Cl^-$, which precipitates from the solution as a yellow solid. The stable pyridinium hydrochloride gives rise to a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 40.27 (in DMSO-d_6) (δ 39.70 in CH_3OD). It is easily deprotonated by NEt_3, leading to the formation of the hydrocarbon-soluble orange complex (dppL)PdCl (**14**; Scheme 3).

Compound **14** was characterized by NMR spectroscopy and by field desorption mass spectroscopy (FD MS). The magnetically equivalent phosphorus nuclei are observed in the $^{31}P\{^1H\}$ NMR spectrum as a singlet at δ 33.07 ($CDCl_3$). In the ^1H NMR spectrum, the phenyl substituents give rise to two sets of resonances, assigned to H_o (δ 7.81) and H_m, H_p (δ 7.36), while the proton in the *ortho* position to the metallated lutidine ring is observed as a singlet at δ 8.21. The methylene protons of the $-CH_2P$ group are observed as a broad singlet at δ 3.90. Its spectroscopic properties are in accord with C_2 symmetry, reported for related Pd complexes possessing a terdentate bis(phosphine) ligand framework.[2L] FD MS shows a base peak at *m/e* 617.

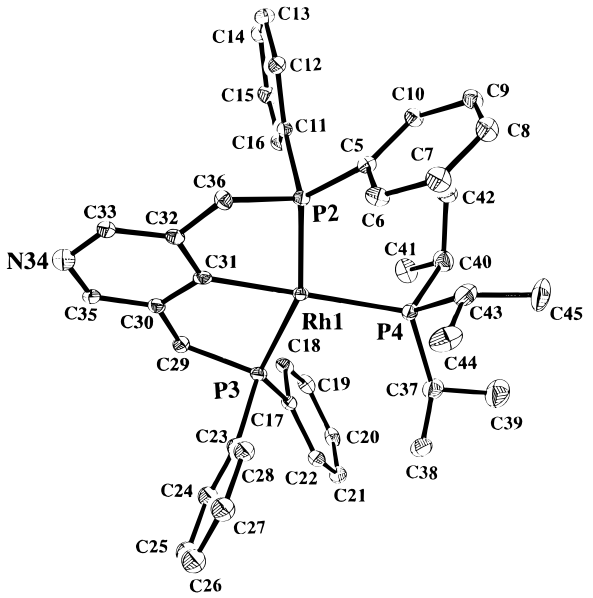


Figure 1. ORTEP drawing of (dppL)RhP^iPr_3 (30% probability level). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Length (Å) and Angles (deg) for (dppL)Rh(P^iPr_3)·C_6H_6

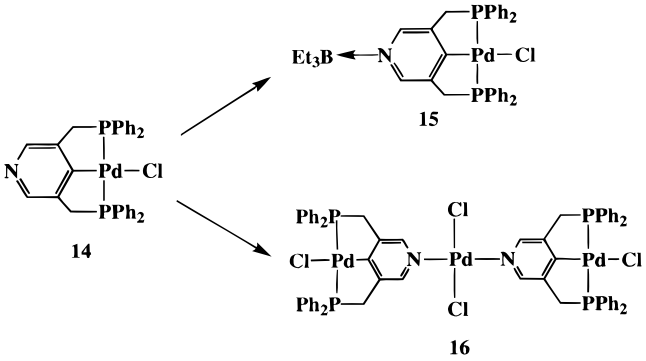
Rh−P(2)	2.269(3)	Rh−P(3)	2.275(3)
Rh−P(4)	2.342(3)	Rh−C(31)	2.065(5)
	Pyridine Ring		
C(30)−C(31)	1.415(5)	C(30)−C(35)	1.380(5)
C(31)−C(32)	1.415(6)	C(32)−C(33)	1.385(5)
C(33)−N(34)	1.338(5)	C(35)−N(34)	1.350(6)
P(2)−Rh−P(3)	157.22(3)	P(2)−Rh−P(4)	101.64(3)
P(3)−Rh−P(4)	101.19(3)	P(2)−Rh−C(31)	78.0(2)
P(3)−Rh−C(31)	79.3(2)	P(4)−Rh−C(31)	179.0(1)
	Pyridine Ring		
C(31)−C(30)−C(35)	120.6(4)	C(30)−C(31)−C(32)	114.2(3)
C(31)−C(32)−C(33)	121.0(4)	C(32)−C(33)−N(34)	124.0(4)
C(33)−N(34)−C(35)	115.9(3)	C(30)−C(35)−N(34)	124.3(4)

(c) Structural Studies. Selected bond distances and angles for **11** are given in Table 2. An ORTEP[15] view of complex **11** is shown in Figure 1. The coordination environment about the Rh(I) center is distorted square planar, having the two phosphorous atoms P(2) and P(3) of the dppL ligand system in the expected *trans* configuration. This P(2)−Rh−P(3) angle is significantly smaller (157.22(3)°) than that reported by Kaska for the P−Rh−P angle in the Rh(III) complex (dtbpx)Rh(H)(Cl) (168.82(8)°) (dtbpx = 1,3-bis(di-*tert*-butylphosphine)-xylene).[2c] The geometric strain imposed on the system by the presence of the two five-membered rings formed upon chelation and the steric congestion about the Rh center due to the bulky P^iPr_3 ligand (Tolman's cone angle 160°)[16] cause a compression of the P(2)−Rh−P(3) angle. The distance of the rhodium to the phosphine *trans* to the heteroaromatic ring (d(Rh−P(4)) = 2.342(3) Å) is significantly elongated compared to Rh−P(2) (2.269(3) Å) and Rh−P(3) (2.275(3) Å) due to the strong *trans* influence of the σ-bonded aryl substituent. Similar effects have been observed before in systems having an orthometallated aromatic ring *trans* to a monophosphine.[2g,n]

It is noteworthy that the pyridine ring retains its planarity. The nitrogen atom is unobstructed and is free to act as a donor to another metal fragment.

(d) Metal Binding Studies. Our structural studies have shown that the nitrogen atom of the lutidine-based ligand is accessible in complex **11** and available for binding to another metal center. Similarly, the spectroscopic properties of complexes **12**−**14** indicate that the nitrogen is exposed and available for binding, allowing the formation of multimetallic aggregates. A multitude of metals form stable and well-characterized complexes with pyridine. We attempted to test our assumption by the reaction of complexes **11**−**14** with $(PhCN)_2PdCl_2$ in a 2:1 stoichiometry. $(PhCN)_2PdCl_2$ is known to undergo facile substitution with pyridine to form stable complexes $(py)_2PdCl_2$.[17] We thought of using **13** possessing the CO *trans* to the aromatic ring for our metal binding studies. Monitoring the ν_{CO} by IR spectroscopy after complex formation would be a good qualitative probe for the electron density on the Rh center.

Scheme 4. Formation of the BEt_3 Adduct **15** and of the Trinuclear Complex **16**



However, the reaction of the Rh-based complexes invariably led to a metallic precipitate, indicating that a more complex redox reaction is taking place. We decided therefore to use the Pd complex **14** in our binding studies and to use ^{13}C NMR spectroscopy to probe the electron density on the Pd center.

To probe the availability of the pyridine nitrogen, we chose to react **14** with a trialkylborane. Trialkylboranes form stable adducts with nitrogen donors, which can be readily identified as being pyridine coordinated by ^{11}B NMR spectroscopy.[18] The reaction of **14** with BEt_3 led to the formation of the expected N-coordination product {(dppL)PdCl}·BEt_3 (**15**). The ^{11}B NMR spectra of the reaction mixture shows the disappearance of the resonance of free Et_3B (δ 87.0) and the appearance of a single resonance for the product at δ 1.5, in a range characteristic for R_3B·py systems. Similar adducts have been reported in the literature (Me_3B·py, δ 0.0 in CH_2Cl_2; Et_3B·py, δ 2.2 in Et_2O).[19] All other spectroscopic results are in accord with Et_3B coordination to the N-donor site of the metalloligand (see Experimental Section).

Compound **14** smoothly reacts with $(PhCN)_2PdCl_2$ in THF to form what appears to be a trinuclear Pd complex (Scheme 4), in which the two (dppL)PdCl moieties coordinate a $PdCl_2$ moiety through the lutidine N. The spectroscopic characteristics of this complex support this assignment.

The molecular weight, as determined by FAB-MS, is 1406.2. The ^1H NMR spectrum of the reaction product is compatible with the formulation of a trinuclear complex. A noteworthy spectroscopic feature is a shift of the *ortho*-protons of the

(15) Johnson, C. K. ORTEP-II, Report ORNL-5138; Oak Ridge National Laboratory: Park Ridge, TN, 1976.
(16) Tolman, C. A. *Chem. Rev.* **1988**, *77*, 313.
(17) Partenheimer, W.; Hoy, E. F. *Inorg. Chem.* **1973**, *12*, 2805.
(18) (a) Nöth, H.; Wrackmeyer, B. *NMR Basic Principles and Progress*; Springer Verlag: Berlin, 1978; Vol. 20, Chapter 7.4.4.2. (b) Wrackmeyer, B. In *Annual Reports in NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1988; Vol. 20, pp 61−203.
(19) Nöth, H.; Wrackmeyer, B. *Chem. Ber.* **1974**, *107*, 3070.

lutidine to lower field upon coordination to the $PdCl_2$ moiety (in **14** H_o at δ 8.21; in **16** H_o at δ 8.58).

In order to get some information about electronic effects of N-coordination, we carried out a vis spectroscopic study of complexes **14**−**16** and the pyridinium complex [H(dppL)-PdCl]$^+$Cl$^-$. A ligand coordinated to the pyridine nitrogen should influence the energy level of the HOMO of the complex and hence should cause a shift of the metal-based transition. N-binding will drain electron density away from the metal center, which will result in a net stabilization of the HOMO. As a result, a transition from the HOMO to the LUMO will require more energy, leading to a hypsochromic shift of the observed transition. The strongest effect is expected for a pyridinium cation. Indeed a weak transition is observed at 406 nm for the pyridinium cation [H(dppL)PdCl]$^+$, which is shifted to lower wavelength (higher energy) compared to the parent **14**. In the N-coordination complexes **15** and **16** only a slight hypsochromic shift is observed (to 420 nm for both complexes). The results from the vis spectroscopic measurements seem to indicate that N-coordination influences the electron density on the metal only to a small extent. However, as van Koten et al.[1d] have shown, ^{13}C NMR spectroscopy is a more sensitive tool for analyzing electronic trends in aryl-bound organometallics.

N-coordination of the metalloligand will effectively result in drainage of electron density from the Pd center of the metalloligand. This should invariably increase the donor ability of the phosphines coordinated to the Pd center and result in a downfield shift in the ^{31}P{^{1}H} NMR compared to the uncomplexed system. The trinuclear complex **16** exhibits a single resonance in the ^{31}P NMR spectrum at δ 34.74 shifted downfield from the starting complex **14** (δ 33.07) by 1.67 ppm. Similarly, the BEt_3 adduct **15** exhibits a single resonance at δ 34.55, indicating drainage of electron density away from the Pd center. ^{13}C NMR shifts are particularly sensitive to changes in electron density in an aromatic system. In a study on ^{13}C NMR shifts in 1,4-disubstituted benzenes, it was shown that a substitutional variations in the *para*-position will greatly influence the ^{13}C shift of the C_{ipso}.[20] Electron-withdrawing substituents in the *para*-position will decrease the electron density on the C_{ipso}, resulting in a downfield shift of its resonance. The ^{13}C shifts of the two ligands dppxH[2i] (**1** with $ER_2 = PPh_2$) and **9** are compared to the Pd complexes **14**−**16** in Table 3.

Introduction of a nitrogen into the aromatic system leads to lower electron density on the carbon atoms. As expected, we observe the appropriate shifts for C_{ipso} (the carbon atom being *trans* to the nitrogen) in the two ligands dppxH (δ 127.0) and dppLH (δ 132.0), indicating that C_{ipso} in dppLH is less electron-rich compared to the all-carbon aromatic system dppxH. Upon coordination to a metal center, this effect is dramatically enhanced. In the parent system (dppx)PdCl,[2i] the PdC_{ipso} is observed at δ 159.0. In (dppL)PdCl (**14**), we observe the PdC_{ipso} of the pyridine ring at δ 170.89 significantly shifted downfield compared to the unsubstituted (dppx)PdCl system. N-coordination should decrease the electron density and should cause a downfield shift of the PdC_{ipso}. This is indeed what is observed. Upon N-coordination of **14** to a $PdCl_2$ moiety a downfield shift to δ 176.89 is observed, clearly indicating the influence of metal binding to the pyridine N on the electron density of a PdC_{ipso} and with this on the Pd center itself. Analogously, N-coordination of BEt_3 causes a downfield shift to δ 177.90. In a study using a series of *para*-substituted NCN-systems, van Koten et al.[1d] have shown that the ^{13}C NMR shift of MC_{ipso} reflects the electron density on the metal center.

Table 3. Selected ^{13}C NMR Data for the Two Ligands dppxH and dppLH (**9**), Complex **14**, the BEt_3 Adduct **15**, and the Trinuclear Pd Complex **16**

	δ C_{ipso}[a]
dppxH	127.0[b,c]
(dppx)PdCl	159.0[b,c]
dppLH	132.0 (**9**)
(dppL)PdCl (**14**)	170.89
{(dppL)PdCl}BEt_3 (**15**)	177.06
{(dppL)PdCl}$_2PdCl_2$ (**16**)	176.89

[a] δ in ppm relative to TMS, in $CDCl_3$. [b] dppx = 1,3-$(Ph_2PCH_2)_2C_6H_3$; dppxH = 1,3-$(Ph_2PCH_2)_2C_6H_4$ (equivalent to **1** where $ER_2 = PPh_2$). [c] Measured by Y. Ben David in our laboratory (value not reported in Venanzi's report on (dppx)PdCl, cf. ref 2i).

Conclusions

With the purpose of a versatile approach to influencing the electron density of a metal center through the backbone of terdentate phosphorous ligands, we designed the bis(phosphine) ligand dppLH based on 3,5-lutidine. After complexation to transition metals, the nitrogen of the pyridine ring is available for binding to a second metal moiety. Our results clearly show that coordination of a metal moiety to the nitrogen of the pyridine ring influences the electron density on the metal center. Hence, the dppL ligand allows us to conveniently change the electronic properties of a metal center by N-coordination. We expect that the coordination of other metal moieties will change the electronic properties of the central metal over a wide range, perhaps allowing one to fine tune its reactivity. As already shown, electronic fine tuning can allow the design of better catalysts.[21] This metalloligand offers also a straightforward approach for the generation of oligo- and multinuclear complexes, as exemplified in the borane adduct **15** and in the trinuclear complex **16**.

Acknowledgment. This work was supported by the Israel Science Foundation, Jerusalem, Israel. We thank the MINERVA Foundation, Munich, Germany, for financial support and for a postdoctoral fellowship to H.-B.K. We thank Dr. R. Fokkens (University of Amsterdam) for carrying out FAB MS and FD MS measurements and Dr. Felix Frolow for the X-ray structure determination.

Supporting Information Available: Tables listing full crystallographic details, atom coordinates, anisotropic temperature factors, H-atom coordinates, and bond lengths and angles and a figure showing the unit cell for **11** (8 pages). Ordering information is given on any current masthead page.

IC951131H

(20) (a) Bromilow, J.; Brownlee, R. T. C.; Lopez, V. O.; Taft, R. W. *J. Org. Chem.* **1979**, *44*, 4766−4770. (b) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429−2438.

(21) Jacobsen, E. N.; Zhang, W.; Guler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703.