Metal Complexes of Mesitylphosphine: Synthesis, Structure, and Spectroscopy

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A series of primary phosphine homoleptic complexes $[ML_4]^{n+}X_n$ (**1**, M = Ni, $n = 0$; **2**, M = Pd, $n = 2$, X = BF_4; **3**, M = Cu, $n = 1$, X = PF_6; **4**, M = Ag, $n = 1$, X = BF_4; L = PH_2Mes, Mes = 2,4,6-$Me_3C_6H_2$] was prepared from mesitylphosphine and $Ni(COD)_2$, $[Pd(NCMe)_4][BF_4]_2$, $[Cu(NCMe)_4]PF_6$, and $AgBF_4$, respectively. Reactions of **1**−**4** with $MeC(CH_2PPh_2)_3$ (triphos) or $[P(CH_2CH_2PPh_2)_3]$ (tetraphos) afforded the derivatives $[M(L')L]^{n+}X_n$ (L′ = triphos; **6**, M = Ni, $n = 0$; **7**, M = Cu, $n = 1$, X = PF_6; **8**, M = Ag, $n = 1$, X = BF_4; L′ = tetraphos; **9**, M = Pd, $n = 2$, X = BF_4). Addition of $NOBF_4$ to **1** yielded the nitrosyl compound $[NiL_3(NO)]BF_4$, **5**. The solution structure and dynamics of **1**−**9** were studied by ^{31}P NMR spectroscopy (including the first reported analyses of a 12-spin system for **1**−**2**). Complexes **1**, **3**, **6**, and **7·solvent** were characterized crystallographically. The structural and spectroscopic studies suggest that the coordination properties of L are dominated by its relatively small cone angle and that the basicity of L is comparable to that of more commonly used tertiary phosphines.

Introduction

Although the coordination chemistry of tertiary and secondary phosphines has been studied in significant detail, little has been reported about the transition-metal chemistry of primary phosphines.[1] The properties of these ligands are expected to differ from those of tertiary phosphines for both steric and electronic reasons. Replacing R in PR_3 by H reduces both the cone angle of the ligand and, because of the relative inductive effect of R and H, the basicity of the phosphorus lone pair. Moreover, in a recent study of the donor strength of a variety of phosphine ligands, Drago found that PH_3 and primary phosphines PH_2R were weaker donors than would be expected if the inductive effect of the hydrogen substituent were the only influence on base strength. The decreased basicity was suggested to be due to the reduced bond angles in primary phosphines (∼90°) in comparison to those in tertiary ones (∼108°); the accompanying change in hybridization gives increased s character in the P lone-pair orbital.[2]

We report here the synthesis of a series of homoleptic complexes of mesitylphosphine (L = PH_2Mes, Mes = 2,4,6-$Me_3C_6H_2$) as well as some derivatives containing tertiary phosphine ligands. We chose to study mesitylphosphine because in comparison to most other primary phosphines it is significantly less air-sensitive and malodorous. The mesityl group makes this ligand sufficiently bulky (cone angle 110°)[3] that a comparison of its coordination chemistry with that of tertiary phosphines should not be completely dominated by steric effects (for comparison, the cone angle of PMe_3 is 118°).[3b] Moreover, the Me groups provide a useful handle for ^{1}H NMR spectroscopy, and the crystal structure of the free ligand has been reported.[4]

Systematic investigations of the coordination behavior of primary phosphines have been hampered by the susceptibility of P−H bonds to metal-mediated cleavage to form phosphido (PHR) or phosphinidene (PR) ligands.[1] The complexes described below do not undergo these reactions—since they do not contain halide coligands, the common dehydrohalogenation[5] reaction is avoided, and they are not sufficiently reactive to add the P−H bond oxidatively.[6] The structural and spectroscopic studies reported here both establish the ligand properties of PH_2Mes at a variety of metal centers and allow direct comparisons of them with those of a more commonly used tertiary phosphine.

Results and Discussion

The homoleptic complexes NiL_4 (**1**), $[PdL_4][BF_4]_2$ (**2**), $[CuL_4]PF_6$ (**3**), and $[AgL_4]BF_4$ (**4**) (Scheme 1) were prepared by displacement of the weakly coordinating ligands cyclooctadiene, acetonitrile, and tetrafluoroborate by mesitylphosphine; complex

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(1) Review: Levason, W. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; John Wiley and Sons: Chichester, England, 1990; Vol. 1; pp 567−641. For selected recent references, see: (a) Ho, J.; Hou, Z.; Drake, R. J.; Stephan, D. W. *Organometallics* **1993**, *12*, 3145−3157. (b) Goerlich, J. R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Polyhedron* **1993**, *12*, 2279−2289. (c) Goerlich, J. R.; Schmutzler, R. *Z. Anorg. Allg. Chem.* **1994**, *620*, 898−907. (d) Bleeke, J. R.; Rohde, A. M.; Robinson, K. D. *Organometallics* **1994**, *13*, 401−403. (e) Ho, J.; Rousseau, R.; Stephan, D. W. *Organometallics* **1994**, *13*, 1918−1926. (f) Blake, A. J.; Champness, N. R.; Forder, R. J.; Frampton, C. S.; Frost, C. A.; Reid, G.; Simpson, R. H. *J. Chem. Soc., Dalton Trans.* **1994**, 3377−3382.

(2) Drago, R. S. *Organometallics* **1995**, *14*, 3408−3417. For a more general discussion of such hybridization effects (Bent's rules), see: (a) Bent, H. A. *J. Chem. Educ.* **1960**, *37*, 616−624. (b) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275−311.

(3) Determined by Tolman's method for unsymmetrical phosphines, see: (a) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53−60. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(4) Bartlett, R. A.; Olmstead, M. M.; Power, P. P.; Sigel, G. A. *Inorg. Chem.* **1987**, *26*, 1941−1946.

(5) For some examples, see: (a) Goldwhite, H.; Hirschon, A. S. *Transition Met. Chem.* **1977**, *2*, 144−149. (b) Issleib, K.; Roloff, H.-R. *Z. Anorg. Allg. Chem.* **1963**, *324*, 250−258. (c) Issleib, K.; Wilde, G. *Z. Anorg. Allg. Chem.* **1961**, *312*, 287−298. (d) Kourkine, I. V.; Chapman, M. B.; Glueck, D. S.; Eichele, K.; Wasylishen, R. E.; Yap, G. P. A.; Liable-Sands, L. M.; Rheingold, A. L. *Inorg. Chem.* **1996**, *35*, 1478−1485.

(6) (a) Powell, J.; Fuchs, E.; Gregg, M. R.; Phillips, J.; Stainer, M. V. R. *Organometallics* **1990**, *9*, 387−393. (b) Ebsworth, E. A. V.; Mayo, R. A. *J. Chem. Soc., Dalton Trans.* **1988**, 477−484. (c) Bonanno, J. B.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1994**, *116*, 11159−11160. (d) Ref 1a.

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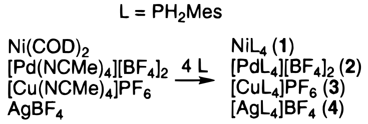
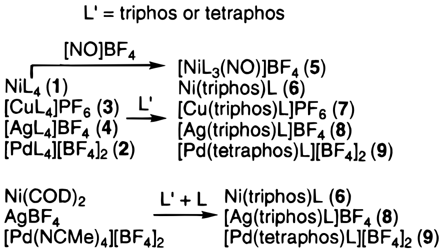
Scheme 1



Scheme 2



1 can also be made by reduction of $[Ni(NCMe)_6][BF_4]_2{\cdot}0.5NCMe$ with an excess of L.[7] The complexes are isolated as white to yellow solids by recrystallization. Compounds **2**−**4** are stable to air and water as solids and in solution, but **1** is air-sensitive.

Complex **1** reacts with $NOBF_4$ (Scheme 2) to yield the purple nitrosyl complex $[NiL_3(NO)]BF_4$ (**5**), which is formulated as a tetrahedral d^{10} Ni(0) species containing linear NO^+. The NO stretching frequency for **5** (1751 cm^{-1}, KBr) is similar to those for the previously reported[8] red $[Ni(triphos)(NO)]^+$ and $[Ni(tep)NO]^+$ [triphos = $MeC(CH_2PPh_2)_3$, tep = $MeC(CH_2PEt_2)_3$], which range from 1750 to 1770 cm^{-1} (Nujol mulls), depending on the counterion. In principle, the NO stretching frequencies should provide information on the relative donor properties of L and these multidentate tertiary phosphines.[9] However, the data suggest that this parameter is insensitive to the electronic nature of the phosphine ligands.

Complexes **1**−**4** react with triphos or tetraphos $[P(CH_2CH_2PPh_2)_3]$ to yield the derivatives Ni(triphos)L (**6**), [Cu(triphos)L]PF_6 (**7**), [Ag(triphos)L]BF_4 (**8**), and [Pd(tetraphos)L]$[BF_4]_2$ (**9**). These substitutions proceed quickly at room temperature, except for the synthesis of **6**, which requires heating at 55 °C for 3 d. Compounds **6** and **8**−**9** can also be prepared by treating the metal precursors with a 1:1 mixture of triphos or tetraphos and L, as shown in Scheme 2. Complexes **5**−**7** and **9** are stable to air and water as solids and in solution.

Compound **8** is stable as a solid but slowly decomposes in CH_2Cl_2 solution by loss of L. The resulting precipitate, identified as Ag(triphos)BF_4 (**10**), could be isolated from the reaction of $AgBF_4$ and triphos in THF/nitromethane. Its $^{31}P\{^1H\}$ NMR spectrum shows two doublets centered at δ 0.3 due to $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ coupling (J = 511 and 591 Hz, respectively). The observed $^1J_{^{107}Ag^{31}P}/^1J_{^{109}Ag^{31}P}$ ratio of 0.865 is in good agreement with that calculated from the gyromagnetic ratios of the Ag nuclei $\gamma(^{107}Ag)/\gamma(^{109}Ag) = 0.870$.[10] These Ag−P coupling constants are similar in magnitude to those reported for Ag(triphos)X (X = NO_3, ClO_4).[11] We assume that **10** contains coordinated BF_4, as in structurally characterized $Cu(PPh_3)_3BF_4$.[12] When complex **10** is treated with L in nitromethane, compound **8** is obtained as shown by ^{31}P NMR spectroscopy.

Table 1. Selected NMR and IR Data for the Mesitylphosphine Complexes[a]

complex	δ ^{31}P	δ ^1H	$^1J_{PH}$	ν_{PH}
PH_2Mes (**L**)	−153.0	3.60	204	2302
NiL_4 (**1**)	−86.5	4.83	283	2278
$[PdL_4][BF_4]_2$ (**2**)	−73.2	5.09	422	2301, 2368
$[CuL_4]PF_6$ (**3**)	−121.0	4.70	317	2357, 2329
$[AgL_4]BF_4$ (**4**)	−131.5	4.62	297	2372
$[NiL_3(NO)]BF_4$ (**5**)	−89.7	5.27	350	2359, 2336
Ni(triphos)L (**6**)	−96.2	6.23	281	2269
[Cu(triphos)L]PF_6 (**7**)	−122.0	5.69	317	2346
[Ag(triphos)L]BF_4 (**8**)	−139.0	4.70	280	2347
[Pd(tetraphos)L]$[BF_4]_2$ (**9**)	−94.5	5.64	381	2301
$BH_3{\cdot}L$ (**11**)	−68.8	4.81	370	2246

[a] NMR data (at 22 °C) in C_6D_6 for **L**, **1**, and **6**, in CD_2Cl_2 for **2**−**5** and **7** and in CD_3NO_2 for **8** and **9**. Chemical shifts are reported in ppm and coupling constants in hertz. IR data (in cm^{-1}) for KBr pellets for **1**−**11** and for a solution of **L** in CH_2Cl_2.

Structure assignments for the mesitylphosphine complexes are consistent with elemental analyses and spectroscopic data. The IR spectra for the complexes show ν_{PH} bands between 2269 and 2372 cm^{-1}.[13] NMR spectroscopy demonstrates changes in the ^{31}P chemical shifts and increases in the $^1J_{PH}$-coupling constant, consistent with primary phosphine coordination.[14] In some cases the ^{31}P and ^1H NMR spectra are not first order, and spectral simulation is required to extract the P−H and other coupling constants, as discussed in more detail below. The NMR and IR data characterizing the P−H bonds in **1**−**9**, in comparison to free L and the borane complex $L-BH_3$ (**11**, prepared from $BH_3{\cdot}THF$ and isolated as white needles, see the Experimental Section for details), are summarized in Table 1.

For complexes **1**−**9**, increase of the $^1J_{PH}$ for PH_2Mes on coordination to the metal centers is consistent with the change in the hybridization of P to sp^3 leading to more s character in the P−H bond.[14] Coordination to BH_3 in **11** gives a similar result. Literature data on a variety of phosphorus compounds show that electronegative substituents X on P increase P−H couplings, an effect rationalized by increased p character in the P−X bonds, which leads to increased s character in the P−H bonds.[15] Our data on the new metal complexes are consistent with these reports. In particular, the largest $^1J_{PH}$ couplings are found for dicationic **2** and **9**, in which the metal center should be the most electron-withdrawing. Comparison of the formally isoelectronic Ni complexes **1** and **5** also fits this trend; the complex with the π-acceptor nitrosyl group exhibits a larger $^1J_{PH}$. The $^1J_{PH}$ values for the Cu(I) and Ag(I) complexes are similar, as expected from the electronegativities of these ions.[16]

If, as expected, the tertiary phosphine ligands in **6**−**9** are better σ donors than the primary phosphines in **1**−**4**, then the ML_3^+ fragment should be less electronegative in **6**−**9** and the P−H coupling should be less than that in **1**−**4**. However, the observed P−H couplings for homoleptic **1**−**4** are very similar to those for the triphos and tetraphos complexes **6**−**9**. These

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(7) The homoleptic secondary phosphine complex $Ni(PHPh_2)_4$ was also prepared by reduction of Ni(II) with excess phosphine. See: Weston, C. W.; Bailey, G. W.; Nelson, J. H.; Jonassen, H. B. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1752−1755.

(8) Berglund, D.; Meek, D. W. *Inorg. Chem.* **1972**, *11*, 1493−1496.

(9) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyls*; Oxford University Press: Oxford, 1992.

(10) Wu, G.; Wasylishen, R. E.; Pan, H.; Liu, C. W.; Fackler, J. P., Jr.; Shang, M. *Magn. Reson. Chem.* **1995**, 734−738.

(11) Camalli, M.; Caruso, F. *Inorg. Chim. Acta* **1990**, *169*, 189−194.

(12) Gaughan, A. P., Jr.; Dori, Z.; Ibers, J. A. *Inorg. Chem.* **1974**, *13*, 1657−1667.

(13) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986.

(14) Verkade, J. G.; Mosbo, J. A. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; pp 425-463.

(15) For some examples, see: (a) Vande Griend, L. J.; Verkade, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 5958−5960. (b) McFarlane, W.; White, R. F. M. *J. Chem. Soc., Chem. Commun.* **1969**, 744. (c) Anderson, D. W. W.; Ebsworth, E. A. V.; Meikle, G. D.; Rankin, D. W. H. *Mol. Phys.* **1973**, *25*, 381−385. See also ref 2 and references therein.

(16) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; HarperCollins: New York, 1993; pp 182−199.

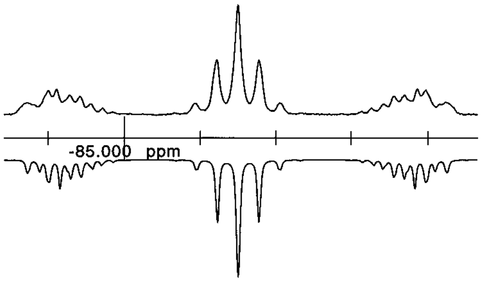

Figure 1. Experimental (top) and simulated (bottom) ^{31}P NMR spectra (22 °C) of Ni(PH$_2$Mes)$_4$ (**1**) in C$_6$D$_6$.

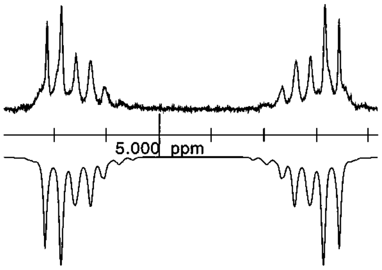

Figure 2. Experimental (top) and simulated (bottom) ^{1}H NMR spectra (22 °C) of Ni(PH$_2$Mes)$_4$ (**1**) in C$_6$D$_6$.

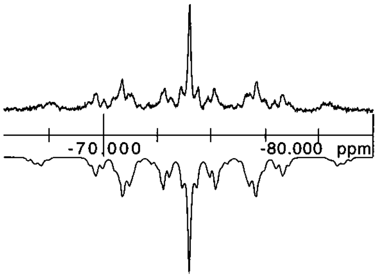

Figure 3. Experimental (top) and simulated (bottom) ^{31}P NMR spectra (22 °C) of [Pd(PH$_2$Mes)$_4$][BF$_4$]$_2$ (**2**) in CD$_2$Cl$_2$.

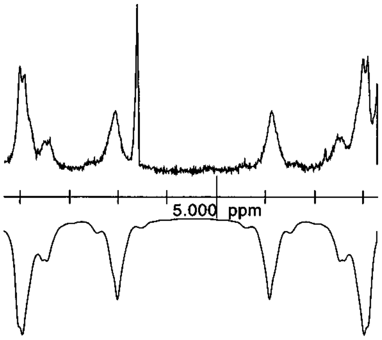

Figure 4. Experimental (top) and simulated (bottom) ^{1}H NMR spectra (22 °C) of [Pd(PH$_2$Mes)$_4$][BF$_4$]$_2$ (**2**) in CD$_2$Cl$_2$. The peak at 5.32 ppm is due to residual protons in the solvent.

observations could be explained in two different ways: either the primary phosphines and tertiary phosphines have similar σ-donor ability or the P−H coupling is insensitive to fine points like the nature of the phosphine ligand and is affected only by large changes in charge at the metal center.

^{31}P NMR spectroscopy provides information on the solution structure and dynamic behavior (intramolecular exchange) of the homoleptic complexes and their derivatives. For the Ni(0) and Pd(II) complexes **1**−**2**, **6**, and **9**, the spectra are consistent either with slow intramolecular exchange of L (on the ^{31}P NMR time scale) or with the complete absence of such an exchange process. The ^{31}P NMR spectra of **1**−**2** show very complex multiplets ($AA'A''A'''X_2X'_2X''_2X'''_2$ spin systems). Using a version of the program Laocoon[17] modified to handle up to 12 spin-$^1/_2$ nuclei, we have successfully simulated these spectra. These simulations also reproduce the experimental ^{1}H NMR resonances due to the PH protons of **1** and **2**. These results allow deduction of the ^{31}P-^{1}H and the ^{31}P−^{31}P coupling constants in **1**−**2**.

The experimental and simulated ^{31}P and ^{1}H NMR spectra of **1** and **2** are shown in Figures 1−4. The results are consistent with the expected geometries: tetrahedral for the Ni(0) complex **1** and square planar for the Pd(II) complex **2**. For **2**, five coupling constants are required: $^1J_{PH} = 422$, $^2J_{PPtrans} = 394$, $^2J_{PPcis} = -30$, $^3J_{PHtrans} = -3$, and $^3J_{PHcis} = 6$ Hz. (The cis and trans $^3J_{PH}$ values were assigned arbitrarily and refined to a good fit with the experimental spectra.) The higher symmetry of complex **1** leads to only three coupling constants: $^1J_{PH} = 283$, $^2J_{PP} = 33$, and $^3J_{PH} = 18$ Hz. We assume that, in both cases, $^4J_{HH}$ is zero, and simulations with $^4J_{HH} = 1-2$ Hz did not affect the spectra.

As expected, the $^2J_{PP}$ coupling in these complexes depends on the P−M−P angle and is greater in **2** than in **1**. Although many homoleptic tertiary phosphine complexes $[ML_4]^{n+}$ are known, $^2J_{PP}$ can rarely be determined. Some $^2J_{PP}$ values, however, have been reported for homoleptic nickel(0)−fluorophosphine complexes[18a−c] and for $[PtL_4]^{2+}$ (L = PMe$_3$, P(OMe)$_3$);[18d] these are similar in magnitude to those found for **1** and **2**, respectively.

The ^{31}P{^{1}H} NMR spectrum of **6** (AX_3 spin system) shows a doublet at δ 9.8 (triphos) and a quartet at δ −96.2 (L) with a small cis coupling constant ($^2J_{PP} = 11$ Hz), which appear as a broad singlet and a broad triplet, respectively, in the ^{31}P NMR spectrum ($^1J_{PH} = 281$ Hz). In the ^{1}H NMR spectrum the PH protons appear at δ 6.23 (C$_6$D$_6$) with an additional $^3J_{PH}$ of 15 Hz.

The ^{31}P{^{1}H} NMR spectrum of **9** (AM_3X spin system) exhibits a doublet at δ 160.2 (tetraphos apical P, $^2J_{PPtrans} = 323$ Hz), a doublet at δ 47.3 (tetraphos equatorial P, $^2J_{PPcis} = 38$ Hz) and a doublet of quartets at δ −94.5 (L). The coupling between the two nonequivalent phosphorus species of the tetraphos is either too small to be observed or, as suggested by a referee, $^3J_{PP}$ (through-backbone) and $^2J_{PP}$ (through-metal) may have equal magnitudes and opposite signs.[19] The PH protons in the ^{1}H NMR spectrum appear as a doublet of multiplets with additional unresolved coupling to the tetraphos P nuclei. For comparison, the ^{31}P{^{1}H} NMR spectrum of the related complex [Pd(tetraphos)P(OMe)$_3$][BF$_4$]$_2$ exhibits two doublets [tetraphos apical P and P(OMe)$_3$, the coupling constant was not reported] and a singlet (tetraphos equatorial P).[20]

In contrast, the ^{31}P NMR spectra of the copper and silver complexes **3**−**4** and **7**−**8**, and nickel nitrosyl complex **5** do not show P−P and long-range P−H couplings like those seen in the nickel and palladium complexes.

The ^{31}P{^{1}H} NMR spectrum of **3** shows a broad peak at δ −121.0 with no observable ^{63}Cu−^{31}P or ^{65}Cu−^{31}P coupling and a sharp septet due to PF$_6$. Improved resolution for the broad Cu−L signal could not be obtained at −60 °C, but at 60 °C (in

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(17) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863−3869.

(18) (a) Crocker, C.; Goodfellow, R. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1687−1689. (b) Lynden-Bell, R. M.; Nixon, J. F.; Schmutzler, R. *J. Chem. Soc. A* **1970**, 565−567. (c) Kruck, T.; Hofler, M.; Jung, H. *Chem. Ber.* **1974**, *107*, 2133−2144. (d) Goodfellow, R. J.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1676−1684.

(19) Crumbliss, A. L.; Topping, R. J. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; pp 531−557.

(20) Aizawa, S.; Funahashi, S. *Chem Lett.* **1994**, 2023−2026.

THF) a singlet, which appeared as a triplet ($^1J_{PH} = 317$ Hz) in the ^{1}H-coupled spectrum, was observed. The chemical shift of this signal did not change with temperature. These results can be explained by rapid intramolecular exchange due to ligand dissociation/reassociation and/or by quadrupolar broadening induced by the $^{63/65}$Cu nuclei in an unsymmetrical environment. Despite such broadening, $^{63/65}$Cu$-^{31}$P coupling in homoleptic phosphine complexes has been observed in high-symmetry environments.[21] For example, $[Cu(PH_2Ph)_4]^+$ shows $^1J_{^{63}Cu^{31}P} = 800$ Hz at 0 °C.[22] We assume that the bulkier mesityl group both increases the rate of dissociation of L and reduces the effective symmetry at Cu in **3**.

Likewise, no ^{63}Cu$-^{31}$P or ^{65}Cu$-^{31}$P coupling was observed in the ^{31}P{^{1}H} NMR spectrum of **7**, which exhibits two broad signals at δ -18.0 (triphos) and -122.0 (L) and a sharp septet (PF_6) between -60 and 40 °C. The chemical shift of these signals did not change with temperature. However, the PH resonances in the ^{1}H NMR spectrum of **7** show an additional $^3J_{PH} = 9$ Hz, which suggests that quadrupolar broadening, not rapid exchange, is responsible for the lack of observed P$-$P coupling.

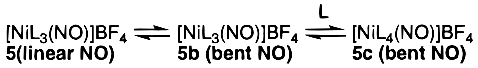
Similarly, no ^{107,109}Ag$-^{31}$P coupling was observed in **4**, whose ^{31}P{^{1}H} spectrum shows a sharp singlet from 20 to -70 °C. In this case, the chemical shift slowly moved downfield (δ 3.4 total) as the temperature was lowered to -70 °C. The ^{31}P{^{1}H} NMR spectrum of **8** exhibits a doublet at δ -15.3 (triphos, $^1J_{AgP} = 197$ Hz) and a broad peak at δ -139.0 (L) at ambient temperature. These observations are consistent with intramolecular exchange of L via dissociation/reassociation equilibria fast on the NMR time scale, as reported for homoleptic Ag(I) complexes of the more sterically demanding ligands P(*p*-Tol)$_3$ and P(OEt)$_3$, which show a temperature-dependent chemical shift and Ag$-$P coupling only at low temperature.[23] The Ag$-$P coupling observed for **8** is similar to that (224$-$230 Hz, depending on the counterion) reported in the tetraphosphine$-$Ag(I) complex [Ag(P(*p*-Tol)$_3$)$_4$]$^+$ at -80 °C.[23]

Compound **5** shows a triplet in the ^{31}P NMR spectrum from 20 to -70 °C with no observable $^2J_{PP}$. The chemical shift of this signal did not change with temperature. This is strikingly different from the behavior of the neutral Ni complexes **1** and **6**. This observation can be explained by the strong labilizing effect of the nitrosyl ligand. Alternatively, reversible isomerization of **5** to a square planar complex with an anionic bent nitrosyl could produce the observed spectra without requiring dissociation of L.

Intermolecular ligand exchange in complexes **1**$-$**9** was studied by ^{31}P NMR spectroscopy at ambient temperature. Addition of L (ca. 4 equiv) to solutions of complexes **1**, **6**, and **9** causes slow ligand exchange on the ^{31}P NMR time scale. The spectrum of a mixture of **1** and L shows two sharp peaks at δ -86.8 (**1**) and -156.8 (L). The spectrum of a mixture of **6** and L shows three sharp peaks at δ 5.2 and -101.0 (coordinated triphos and L in **6**) and at δ -156.8 (L). For **9**, the ^{31}P{^{1}H} NMR spectrum shows signals at δ 157.5, 44.5, and -94.0 due to **9** and at δ -157.3 (L). Ligand substitution does occur in **1**, **6**, and **9** as shown by the rapid (minutes) exchange of bound PH_2Mes on addition of PD_2Mes; these reactions could also be conveniently monitored by ^{31}P NMR.

Faster ligand exchange on the ^{31}P NMR time scale was observed in similar experiments with complexes **2**$-$**5** and **7**$-$**8**. In several cases, only one peak due to mesitylphosphine, with an average chemical shift between that of free and coordinated L, was observed. A solution containing **2** and a trace of L showed only one signal at δ -90, which broadened considerably on addition of more L, consistent with rapid ligand exchange. Likewise, a mixture of **3** and L shows a broad peak at δ -130.0 and a sharp peak for the PF_6 anion (δ -141.5), and similar results are obtained for **4** (δ -145.9, sharp) and **8** [δ -13.5 (d, $^1J_{AgP} = 197$ Hz, triphos); δ -150.1 (L)]. For **7** + L, the observed peaks both for the complex (δ -17.1 and -125.0) and for L (δ -154.9) broaden and change slightly in chemical shift (the signals due to free and coordinated L move toward each other) while the PF_6 signal (δ -141.5) remains sharp. These observations are consistent with ligand exchange occurring at an intermediate rate on the NMR time scale.

Scheme 3



$$\underset{\textbf{5(linear NO)}}{[NiL_3(NO)]BF_4} \rightleftharpoons \underset{\textbf{5b (bent NO)}}{[NiL_3(NO)]BF_4} \xrightleftharpoons{L} \underset{\textbf{5c (bent NO)}}{[NiL_4(NO)]BF_4}$$

In contrast, a mixture of **5** and 5 equiv of L exhibits a sharp peak at δ -87.3 ($^1J_{PH} = 350$ Hz, **5**) and a broad peak at δ -102.6. Use of 10 equiv of L changes the chemical shift of **5** slightly (to δ -90.3, t, $^1J_{PH} = 350$ Hz) and that of the broad peak more (to δ -149.3, with further broadening.) In addition to peaks due to the Mes group, the ^{1}H NMR spectrum of this mixture shows a PH peak due to **5** at δ 5.30 (dm, $^1J_{PH} = 350$ Hz). At -70 °C, an additional PH resonance (δ 3.82, broad d, $^1J_{PH} = 228$ Hz) can be observed; this corresponds to a broad triplet in the ^{31}P NMR spectrum [δ -142.0 ($^1J_{PH} = 228$ Hz)]. At this temperature, the ^{31}P NMR signal due to **5** is observed at δ -85.6 (t, $^1J_{PH} = 350$ Hz). These results are consistent with intermolecular exchange of **5** with L at an intermediate rate on the NMR time scale; the mechanism of exchange is considered in more detail below.

These results are consistent with the observations on intramolecular exchange and with the expected mechanisms for intermolecular ligand substitution in these complexes. The simplest cases are **1**, **6**, and **9**, where the dissociative step expected for substitution is slow on the NMR time scale, and **3**, **4**, and **8**, where it is fast. The intermediate rate of exchange observed for **7** is also consistent with its spectra in the absence of added L. The rapid intermolecular substitution observed for square planar **2** is consistent with the associative mechanism expected for this reaction.

The results for **5** are somewhat more complicated and may be explained by the previously discussed reversible isomerization of **5** to a square planar species with a bent nitrosyl ligand (**5b**). Intermolecular exchange could then occur by an associative mechanism via the five-coordinate bent nitrosyl complex $[NiL_4(NO)][BF_4]$ (**5c**, Scheme 3). The broad peak observed on addition of L to **5** could then be due to rapid exchange of L with **5c**, while rapid intramolecular isomerization of **5** and **5b** accounts for the lack of observed P$-$P and long-range P$-$H coupling in **5**. The IR spectrum of **5** in CH_2Cl_2 shows a peak at 1818 cm^{-1} with a shoulder at 1788 cm^{-1}; this signal, like the one at 1751 cm^{-1} in KBr, is assigned to a linear NO. A similar solution containing 10 equiv of added L produces an additional peak at 1444 cm^{-1}, which may be assigned to the proposed bent NO ligand in **5c**.[9] The previously reported equilibrium between $[NiH(PEt_3)_3]^+$ and $[NiH(PEt_3)_4]^+$, which could also be observed by NMR, provides a precedent for this proposed mechanism.[24]

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(21) King, R. W.; Huttemann, T. J.; Verkade, J. G. *J. Chem. Soc., Chem. Commun.* **1965**, 561.

(22) Black, J. R.; Levason, W.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1993**, 3129$-$3136.

(23) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386$-$6391.

(24) English, A. D.; Meakin, P.; Jesson, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 422$-$436.

Table 2. Crystallographic Data for **3**, **1**, **7·(solvent)**, and **6**

	3	**1**	**7·solvent**	**6**
formula	$C_{36}H_{52}CuF_6P_5$	$C_{36}H_{52}NiP_4$	$C_{50}H_{52}CuF_6P_5$	$C_{50}H_{52}P_4Ni$
fw	817.2	667.4	1009.3	835.51
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, Å	11.842(3)	18.584(4)	19.780(3)	9.587(1)
b, Å	11.891(2)	11.506(3)	13.853(2)	11.528(1)
c, Å	16.486(4)	18.965(4)	18.743(4)	22.194(2)
α, deg	72.62(2)			102.314(7)
β, deg	79.17(2)	115.84(5)	90.20(1)	90.921(9)
γ, deg	68.14(2)			114.15(1)
V, Å^3	2048.3(9)	3650(2)	5136(1)	2172.0(4)
z	2	4	4	2
cryst color	colorless	yellow-green	colorless	yellow-orange
D(calc), g cm^{-3}	1.325	1.215	1.305	1.278
μ(Mo Kα), cm^{-1}	7.80	7.30	6.36	6.28
T, K	296	252	298	293
radiation		Mo Kα (λ =0.710 73 Å)		
$R(F)$, %	5.94[a]	9.00[a]	8.94[b]	4.14[b]
$R(wF)$, %	7.59	10.64	14.96[c]	10.75[c]

[a] Quantity minimized = $\sum w\Delta^2$; $R = \sum\Delta/\sum(F_o)$; $R(w) = \sum\Delta w^{1/2}/\sum(F_o\, w^{1/2})$, $\Delta = |(F_o - F_c)|$. [b] Quantity minimized = $R(wF^2) = \sum[w(F_o^2 - F_c^2)^2]/\sum[(wF_o^2)^2]^{1/2}$; $R = \sum\Delta/\sum(F_o)$, $\Delta = |F_o - F_c|$. [c] $R(wF^2)$, %.

These NMR results on the dynamic behavior and ligand substitution reactions of the mesitylphosphine complexes correlate well with those reported in the literature for phosphine complexes of Ni(0), Cu(I), and Ag(I) and reflect the small size of L. As shown by Tolman,[3a] phosphine dissociation in Ni(PR$_3$)$_4$ complexes is controlled by sterics; larger ligands dissociate more readily. The behavior of complexes **1** and **6** is similar to that of Ni(PMe$_3$)$_4$, in which slow ligand dissociation on the NMR time scale is demonstrated by the observation of ^{61}Ni−^{31}P coupling.[25] Similar results, such as the slow intramolecular ligand exchange at low temperature in [Cu(PMe$_3$)$_4$]$^+$ and [Cu(PH$_2$Ph)$_4$]$^+$ were observed in earlier studies of Cu(I) complexes.[22] The rapid intra- and intermolecular phosphine exchange in silver complexes **4** and **8** is similar to that reported by Muetterties in [AgL$_4$]$^+$ [L = P(OEt)$_3$, P(p-Tol)$_3$].[23] Although homoleptic Pd(II) phosphine complexes, such as [Pd(PPh$_3$)$_4$]$^{2+}$ and the triphenylphosphite analog, have been reported,[26] information on their ligand substitution reactions is lacking.

Complementary information on the coordination properties of L was obtained by structural characterization of compounds **1**, **3**, **6**, and **7·solvent** by X-ray crystallography. Crystal, data collection, and refinement parameters are given in Table 2. ORTEP diagrams are shown in Figures 5−8. Tables 3 and 4 contain selected bond lengths and angles. Further details of the structure determinations are given in the Experimental Section and the Supporting Information.

To our knowledge, the only primary phosphine homoleptic complexes reported previously are [Cu(PH$_2$Ph)$_4$]$^{+22}$ and {Cu-[1,2(PH$_2$)$_2$C$_6$H$_4$]$_2$}$^+$;[27] the isoelectronic Ni(0) and Cu(I) complexes **1** and **3** are the first ones to be structurally characterized.

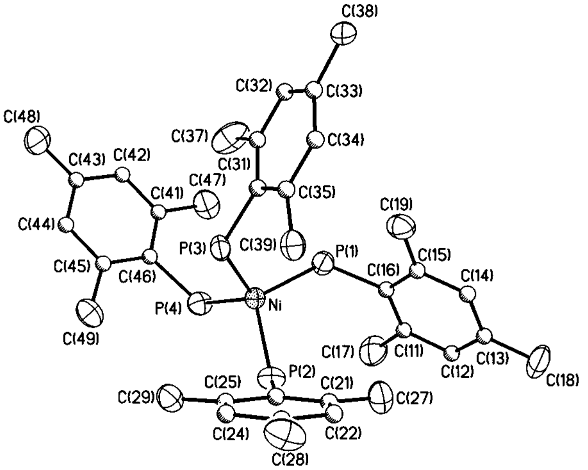

Figure 5. ORTEP drawing of [Ni(PH$_2$Mes)$_4$] (**1**), with 35% thermal ellipsoids. Phenyl ring carbons were refined anisotropically, and hydrogens have been removed for clarity.

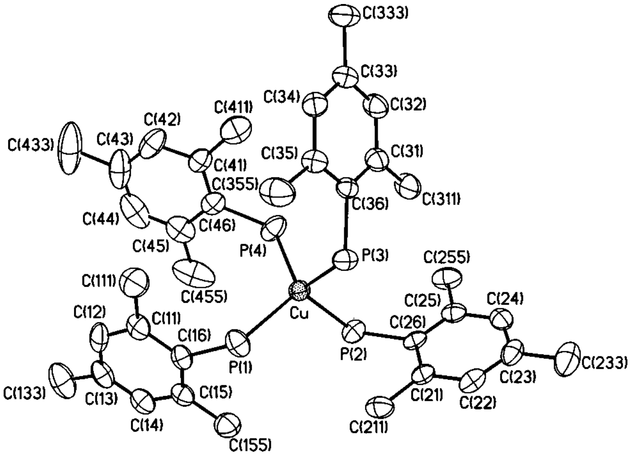

Figure 6. ORTEP drawing of [Cu(PH$_2$Mes)$_4$]PF$_6$ (**3**), with 35% probability thermal ellipsoids. The anion is not shown, and hydrogens have been removed for clarity.

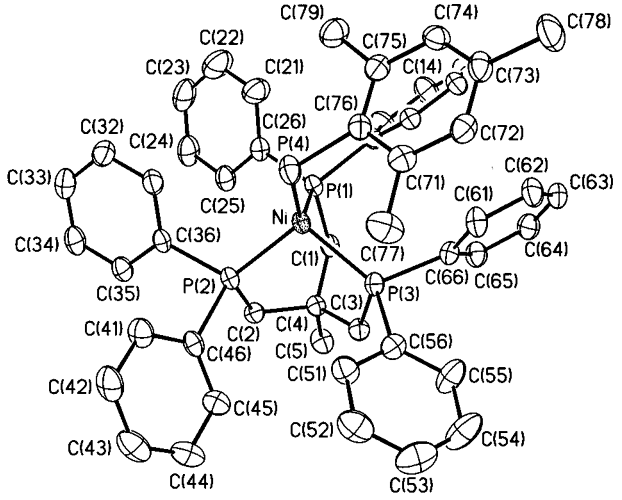

Figure 7. ORTEP drawing of Ni(triphos)PH$_2$Mes (**6**), with 35% probability thermal ellipsoids. Hydrogens have been removed for clarity.

Despite the large number of homoleptic nickel−phosphine complexes NiL$_4$, surprisingly few crystal structures are known.[28] Consistent with the solution NMR data, complex **1** is tetrahedral in the solid state, with an average Ni−P bond length of 2.149(8) Å and Ni−P−Ni angles ranging from 106.9(3)° to 111.3(2)°. Complex **3** shows distorted tetrahedral geometry with two sets of Cu−P distances [2.269(2) and 2.271(2) Å, 2.298(3) and 2.295(2) Å] and P−Cu−P angles ranging from 104.0(1)° to 116.5(1)°. The solution NMR data described above suggest that the four phosphine ligands are equivalent in solution, so these distortions may be a consequence of crystal packing forces.

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(25) Avent, A. G.; Cloke, F. G. N.; Day, J. P.; Seddon, E. A.; Seddon, K. R.; Smedley, S. M. *J. Organomet. Chem.* **1988**, *341*, 535−541.

(26) Yamazaki, S. *Inorg. Chem.* **1982**, *21*, 1638−1640.

(27) (a) Wild, S. B. *Pure Appl. Chem.* **1990**, *62*, 1139−1144. (b) Kang, Y. B.; Pabel, M.; Pathak, D. D.; Willis, A. C.; Wild, S. B. *Main Group Chem.* **1995**, *1*, 89−98.

(28) Hursthouse, M. B.; Izod, K. J.; Motevalli, M.; Thorton, P. *Polyhedron* **1994**, *13*, 151−153.

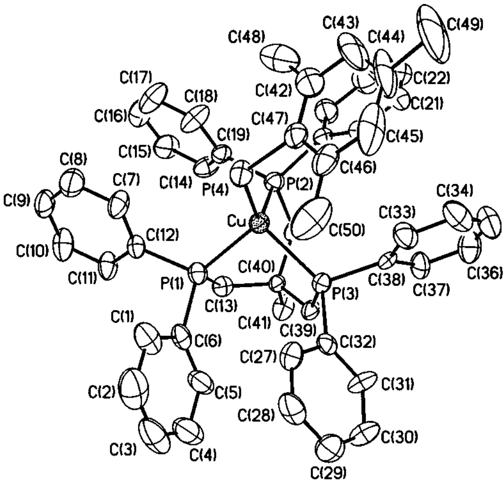

Figure 8. ORTEP drawing of [Cu(triphos)PH_2Mes]PF_6 (**7·solvent**), with 35% probability thermal ellipsoids. The anion and apparent solvent are not shown, and hydrogens have been removed for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Homoleptic Mesitylphosphine Complexes

complex	NiL_4 (**1**)	[CuL_4]PF_6 (**3**)
M−P	2.142(7)	2.271(2)
	2.156(7)	2.295(2)
	2.158(7)	2.298(3)
	2.140(8)	2.269(2)
P−C	1.803(13)	1.795(9)
	1.837(11)	1.799(8)
	1.840(10)	1.820(6)
	1.819(13)	1.806(7)
P−M−P	111.2(3)	113.5(1)
	111.3(2)	104.6(1)
	109.5(2)	106.5(1)
	108.6(2)	116.5(1)
	109.2(2)	104.0(1)
	106.9(3)	111.5(1)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Mixed Triphos Mesitylphosphine Complexes

complex	Ni(triphos)L (**6**)	[Cu(triphos)L]PF_6 (**7·solvent**)
M−P (L)	2.1448(12)	2.241(3)
M−P (triphos)	2.1361(9)	2.279(3)
	2.145(1)	2.289(3)
	2.168(1)	2.262(3)
P−C (L)	1.857(2)	1.812(6)
P−C (Ph−triphos)	1.839(2)	1.811(5)
	1.867(2)	1.818(6)
	1.848(2)	1.817(5)
	1.864(2)	1.839(5)
	1.846(2)	1.820(5)
	1.850(2)	1.828(5)
P−C (CH_2−triphos)	1.873(4)	1.868(8)
	1.870(4)	1.859(8)
	1.866(3)	1.858(8)
P−M−P (L)	117.01(4)	119.5(1)
	117.03(4)	118.6(1)
	125.72(4)	125.8(1)
P−M−P (triphos)	101.08(4)	94.6(1)
	94.82(4)	97.2(1)
	96.16(4)	94.13(9)

Comparison of these structures with those of other homoleptic phosphine complexes suggests that the M−P bond lengths are controlled by the steric bulk of the phosphine ligand, as well as its donor properties. The Ni−P bond lengths in **1** [av = 2.149(8) Å] and the related compounds $Ni(PF_3)_4$ [Ni−P = 2.099(3) Å][29] and $Ni(PEt_3)_4$ [av Ni−P = 2.2125(10) Å][28] correlate with the phosphine cone angles (PH_2Mes, 110°; PF_3, 104°; PEt_3, 132°).[3] As pointed out by a referee, this comparison is more meaningful for the PH_2Mes and PEt_3 complexes, since the short Ni−P bond distance in $Ni(PF_3)_4$ is likely a result of the π-acceptor properties of PF_3. Similarly, the average Cu−P bond length in **3** of 2.28 Å is similar to that of the good σ-donor ligand PMe_3 in $[Cu(PMe_3)_4]^+$ (av = 2.26 Å, PMe_3 cone angle 118°)[30] and smaller than that in the more hindered $[Cu(PPh_3)_4]^+$ [av = 2.56 Å,[31] PPh_3 cone angle 145°].[32]

On the basis of effective nuclear charge of the d^{10} species Cu(I) and Ni(0), the Cu−P bonds in **3** would be expected to be shorter than the Ni−P ones in **1**. Observation of the opposite result suggests that the Ni−L interaction is stronger than the Cu−L one; this may be attributed to π-back-bonding interactions in the Ni, but not in the Cu complex.[33] Orpen reported that such interactions in PPh_3 complexes led to increases in P−C bond length and attributed this to occupation of P−C antibonding orbitals.[34] The P−C bond lengths in **1** range from 1.803(13) to 1.840(10) Å—not significantly different from the P−C bond length in the free phosphine [1.807(5) Å].[4] However, a similar trend is observed in the triphos complexes **6** and **7**. The Ni−P(L) bond length in **6** of 2.145(1) Å is significantly shorter than the Cu−P(L) bond length in **7** (2.241(3) Å). In this case, moreover, the P−C bond length in Ni-coordinated mesitylphosphine [1.857(2) Å] is significantly longer than that in the free phosphine, which is similar to that in the copper complexes **3** [av = 1.805(9) Å] and **7** [1.812(6) Å].

A similar trend is apparent in the triphos complexes **6** and **7**. The Ni−P (triphos) bond length [av = 2.1496(11) Å] is significantly shorter than the Cu−P one [av = 2.277(3) Å], and the P−C(Ar) bonds in the triphos ligand are elongated in **6** [av = 1.852(2) Å] but not in **7** [av = 1.822(6) Å]. These results suggest that a Ni−triphos back-bonding interaction in **6** is also important.

Comparison of the M−L bond lengths in the structures of the homoleptic and the triphos complexes suggest that bonding of L to the three-coordinate fragments $[ML_3]^{n+}$ and $[M(triphos)]^{n+}$ is similar, despite the steric and electronic differences of the supporting ligands. For example, the Ni−PH_2Mes distance in **6** [2.1448(12) Å] and the Cu−PH_2Mes distance in **7** [2.241(3) Å] are similar to those in the homoleptic **1** (av = 2.149(8) Å) and **3** [av = 2.283(3) Å], respectively. These results are consistent with the observations of very similar P−H and P−P couplings in **1** and **6** observed by the NMR studies described above.

The geometries of the triphos ligands in **6** and **7** are normal. The Ni−P distance and the P−Ni−P angle for the triphos in **6** (2.1496(11) Å and 97.35(4)° average) do not differ much from those in the complex Ni(triphos)SO_2 [2.205(3) Å and 94.9(1)° average].[35] Likewise, the Cu−P distance and the P−Cu−P angle for the triphos in **7** [2.2767(3) Å and 95.34(10)° average]

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(29) (a) Almenningen, A.; Andersen, B.; Astrup, E. E. *Acta Chem. Scand.* **1970**, *24*, 1579. (b) Marriot, J. C.; Salthouse, J. A.; Ware, M. J.; Freeman, J. M. *J. Chem. Soc., Chem. Commun.* **1970**, 595.

(30) Dempsey, D. F.; Girolami, G. S. *Organometallics* **1988**, *7*, 1208−1213.

(31) Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 125−133.

(32) (a) McAuliffe, C. A. in *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2; pp 1012−1029. (b) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.

(33) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760−765.

(34) (a) Orpen, A. G.; Connelly, N. G. *Organometallics* **1990**, *9*, 1206−1210. (b) Dunne, B. J.; Morris, R. B.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 653−661.

(35) Dapporto, P.; Midollini, S.; Orlandini, A.; Sacconi, L. *Inorg. Chem.* **1976**, *15*, 2768−2774.

are comparable to those in Cu(triphos)Ph [2.304(2) Å and 92.0(1)°][36] and Cu(triphos)(BH_4) [2.303(3) Å and 94.0(1)° average].[37]

Conclusion. We have prepared and characterized a series of metal complexes of mesitylphosphine and used X-ray crystallography and NMR spectroscopy to examine its ligand properties in the absence of P−H bond cleavage reactions. As expected, the small cone angle of L reduces the rate of ligand dissociation in the complexes in comparison to larger phosphines, and the $^1J_{PH}$ coupling constants can be used to gauge the electronegativity of the metal center. The X-ray structural studies are consistent with a Ni−L π-back-bonding interaction. The data do not offer conclusive information on the relative donor abilities of L and those of the more commonly used tertiary phosphines. Comparison of the NMR properties and structural parameters in homoleptic **1** and **3** and triphos complexes **6** and **7** suggests that the basicity of triphos is similar to that of three mesitylphosphines. However, it is not clear if changes in parameters like J_{PP}, J_{PH}, and M−P bond distance are a good measure of ligand donor ability. More structural and spectroscopic studies including other primary phosphines and metal centers will be required to see if these results are general and to further develop the coordination chemistry of primary phosphines.

Experimental Section

General Experimental Details. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under a nitrogen atmosphere at 20°C in a drybox or using standard Schlenk techniques. Petroleum ether (bp 38−53 °C), ether, THF, and toluene were dried over and distilled from Na/benzophenone before use. CH_2Cl_2 was distilled from CaH_2. Nitromethane (spectrochemical grade, Aldrich) was used as received.

NMR spectra were recorded on a Varian 300 MHz spectrometer. ^1H or ^{13}C NMR chemical shifts are reported vs Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{31}P NMR chemical shifts are reported vs H_3PO_4 (85%) used as an external reference. Coupling constants are reported in hertz. Unless otherwise noted, peaks in NMR spectra are singlets. IR (KBr) spectra were recorded on a Perkin-Elmer 1600 series FTIR machine and are reported in cm^{-1}. Elemental analyses were provided by Schwarzkopf Microanalytical Laboratory.

The NMR simulations were performed on an IBM RS/6000-580 workstation using a version of Laocoon 3 which has been modified to handle up to 12 spin-$^1/_2$ nuclei. Full details will be reported separately.

Unless otherwise noted, reagents were from commercial suppliers. The following compounds were made by the literature procedures: PH_2Mes,[38] $[Pd(NCMe)_4][BF_4]_2$,[39] $[Cu(NCMe)_4][PF_6]$,[40] and $[Ni(NCMe)_6][BF_4]_2\cdot 0.5NCMe$.[41] PD_2Mes was prepared from PCl_2Mes and $LiAlD_4$.[5d]

Ni(PH$_2$Mes)$_4$ (1). To a yellow solution of $Ni(COD)_2$ (150 mg, 0.55 mmol) in THF (4 mL) was added a solution of PH_2Mes (415 mg, 2.73 mmol) in THF (2 mL), and the resulting mixture was stirred overnight. The volume of the solvent was reduced to 2 mL, petroleum ether was layered on top, and the cooling of the solution to −20 °C gave 240 mg (66% yield) of air-sensitive pale-green needles.

Anal. Calcd for $C_{36}H_{52}NiP_4$: C, 64.78; H, 7.87. Found: C, 64.64; H, 8.07. IR: 2959 (s), 2914 (s), 2278 (s), 1603 (s), 1560, 1463 (s), 1371, 1148, 1059 (s), 1025 (s), 861 (vs), 840 (vs), 702, 627, 612, 570, 546 cm^{-1}. ^1H NMR (C_6D_6): δ 6.69 (8H, Ar), 4.83 (8H, m, PH_2), 2.17 (24H, *o*-CH_3), 2.12 (12H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.2 (Ar), 136.4 (Ar), 129.1 (p Ar), 21.8 (CH_3), 21.4 (CH_3). The expected fourth Ar peak was not observed for complexes **1**−**3** and **5**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −86.5. ^{31}P NMR (C_6D_6): δ −86.5 (m).

Alternatively, in an NMR scale experiment, to a solution of $[Ni(NCMe)_6][BF_4]_2\cdot 0.5NCMe$ (20 mg, 0.04 mmol) in CH_3NO_2 (1 mL) was added PH_2Mes (40 mg, 0.25 mmol) to afford a yellow solution. ^{31}P NMR spectroscopy showed that complex **1** was formed.

[Pd(PH$_2$Mes)$_4$][BF$_4$]$_2$ (2). To a solution of $[Pd(NCMe)_4][BF_4]_2$ (150 mg, 0.34 mmol) in CH_3NO_2 (3 mL) was added PH_2Mes (260 mg, 1.69 mmol) dissolved in CH_3NO_2 (1 mL), and the mixture was stirred overnight. During this time a pale-yellow solid precipitated. The CH_3NO_2 solution was decanted, and the solid was recrystallized from CH_2Cl_2/Et_2O at −20 °C to give 120 mg (40% yield) of the pale-yellow product. Anal. Calcd for $C_{36}H_{52}B_2F_8P_4Pd\cdot 0.54CH_2Cl_2$: C, 46.79; H, 5.72. Found: C, 46.67; H, 5.83. The amount of cocrystallized CH_2Cl_2 was confirmed by integration of the ^1H NMR spectrum. IR: 3050, 2969, 2915, 2368, 2301, 1603 (s), 1560, 1452 (s), 1378, 1055 (s, broad), 889 (s), 851 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.06 (8H, Ar), 5.09 (8H, m, PH_2), 2.38 (24H, *o*-CH_3), 2.32 (12H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 144.9 (Ar), 143.1 (Ar), 130.9 (Ar), 22.9 (CH_3), 21.6 (CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −73.2. ^{31}P NMR (CD_2Cl_2): δ −73.2 (m).

[Cu(PH$_2$Mes)$_4$]PF$_6$ (3). To an off-white slurry of $[Cu(NCMe)_4][PF_6]$ (500 mg, 1.34 mmol) in THF (3 mL) was added PH_2Mes (860 mg, 5.63 mmol), and the resulting mixture was stirred overnight, during which time a pink solid precipitated. The THF solution was decanted, and the solid was washed with petroleum ether (2 × 5 mL). The compound was recrystallized from THF/petroleum ether at −20 °C to give 450 mg (45% yield) of pale-pink needles. Anal. Calcd for $C_{36}H_{52}CuF_6P_5$: C, 52.90; H, 6.43. Found: C, 53.28; H, 6.41. IR: 3050, 2915 (s), 2736, 2357 (s), 2329 (s), 1602 (s), 1557(m), 1377 (s), 1294, 1083 (s), 1026 (s), 856 (s, broad), 702 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.78 (8H, Ar), 4.70 (8H, d, $^1J_{PH}$ = 317 Hz, PH_2), 2.45 (12H, *p*-CH_3), 2.03 (24H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.3 (Ar), 140.0 (Ar), 129.8 (Ar), 22.6 (CH_3), 21.3 (CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −121.0 (broad), −141.5 (septet, $^1J_{PF}$ = 711 Hz).

[Ag(PH$_2$Mes)$_4$]BF$_4$ (4). To $AgBF_4$ (50 mg, 0.26 mmol) was added a solution of PH_2Mes (164 mg, 1.08 mmol) in THF (4 mL), and the resulting mixture was protected from light and stirred for 4 h. The solvent was removed, and the off-white residue was washed with petroleum ether (3 × 1 mL) and dried in vacuo to give 145 mg (70% yield) of the white product, which slowly decomposes in solution. An analytical sample was obtained by recrystallization from CH_2Cl_2/Et_2O. Anal. Calcd for $C_{36}H_{52}AgBF_4P_4$: C, 53.82; H, 6.53. Found: C, 53.33; H, 6.53. Repeated analyses gave consistently low results for carbon. We believe this is due to decomposition as described above. IR: 2961, 2372, 1732, 1603 (s), 1559, 1457 (s), 1375, 1294, 1170, 1035 (s). ^1H NMR (CD_2Cl_2): δ 6.85 (d, $^4J_{PH}$ = 3, Hz, 8H, Ar), 4.62 (d, $^1J_{PH}$ = 297 Hz, 8H, PH_2), 2.28 (24H, *o*-CH_3), 2.11 (12H, *p*-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.1(d, J_{PC} = 9 Hz, Ar), 139.7 (Ar), 129.5 (d, J_{PC} = 6 Hz, Ar), 118.8 (d, J_{PC} = 23 Hz, Ar), 22.5 (d, J_{PC} =11 Hz, CH_3), 21.1 (CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −131.5. ^{31}P NMR (CD_2Cl_2): δ −131.5 (t, $^1J_{PH}$ = 297 Hz).

[Ni(PH$_2$Mes)$_3$(NO)]BF$_4$ (5). To a pale-green solution of $Ni(PH_2Mes)_4$ prepared in situ by mixing $Ni(COD)_2$ (30 mg, 0.1 mmol) and PH_2Mes (68 mg, 0.45 mmol) in THF (2 mL) was added $NOBF_4$ (15 mg, 0.13 mmol) to afford a purple solution. The solvent was removed, and the residue was washed with petroleum ether (2 × 5 mL) and dried to give 56 mg (80% yield) of the product. The complex can be recrystallized from a dilute solution in CH_2Cl_2/diethyl ether. Anal. Calcd for $C_{27}H_{39}BF_4NNiOP_3$: C, 51.30; H, 6.23; N, 2.21. Found: C, 51.14; H, 6.52; N, 1.90. IR: 2936 (vs), 2854 (vs), 2359, 2336, 1751 (broad, s), 1605 (s), 1558 (s), 1456 (broad, s), 1374 (s), 1113 (s), 847 (s), 702, 620 cm^{-1}. ^1H NMR (CD_2Cl_2): δ 6.93 (6H, Ar), 5.27 (6H, dm, $^1J_{PH}$ = 350 Hz, PH_2), 2.30 (9H, *p*-CH_3), 2.19 (18H, *o*-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 141.4 (Ar), 140.6 (Ar), 130.0 (Ar), 22.2 (CH_3), 21.2 (CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ −89.7. ^{31}P NMR (CD_2Cl_2) δ −89.7 (t, $^1J_{PH}$ = 350 Hz).

Ni(triphos)PH$_2$Mes (6). A green mixture of $Ni(PH_2Mes)_4$ (200 mg, 0.3 mmol) and triphos (187 mg, 0.3 mmol) was heated in THF (10 mL) at 55 °C for 3 d. The solvent was removed, and the product was

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(36) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1984**, *3*, 1444−1445.

(37) Ghilardi, C. A.; Midolini, S.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4096−4098.

(38) (a) Oshikawa, T.; Yamashita, M. *Chem. Ind. (London)* **1985**, 126−127. (b) Reference 4.

(39) Thomas, R. R.; Sen, A. *Inorg. Synth.* **1990**, *28*, 63−67.

(40) Kubas, G. J. *Inorg. Synth.* **1979**, *14*, 68−71.

(41) Hathaway, B. J.; Holah, D. G.; Underhill, A. E. *J. Chem. Soc.* **1962**, 2444−2448.

recrystallized from petroleum ether (10 mL) to afford 160 mg (72% yield) of a yellow solid.

Alternatively, a mixture of $Ni(COD)_2$ (100 mg, 0.36 mmol), triphos (227 mg, 0.36 mmol), and PH_2Mes (72 mg, 0.47 mmol) in THF (20 mL) was heated at 60 °C for 4 d. The solvent was removed, and the residue was recrystallized from petroleum ether to give 200 mg (66% yield) of the product.

Anal. Calcd for $C_{50}H_{52}NiP_4$: C, 71.87; H, 6.29. Found: C, 70.45; H, 6.50. Repeated analyses, even on crystals from the batch used for X-ray crystallography, gave consistently low results for carbon. IR: 3050, 2918, 2269, 1480, 1434 (vs), 1183, 1118, 1096 (s), 1026, 998, 882, 847, 738 (s), 695 (vs), 566, 515 (vs) cm^{-1}. ^1H NMR (C_6D_6): δ 7.22 (12H, m, Ar), 6.81 (20H, m, Ar), 6.23 (2H, d quart, $^1J_{PH} = 281$ Hz, $^3J_{PH} = 15$ Hz, PH_2), 2.60 (6H, CH_2), 2.25 (6H, d, $^4J_{PH} = 6$ Hz, o-CH_3), 2.18 (3H, p-CH_3), 1.21 (3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 142.9 (m, Ar), 139.0 (d, $J_{PC} = 8$ Hz, Ar), 136.3 (Ar), 131.9 (m, Ar), 129.1 (d, $J_{PC} = 5$ Hz, Ar), 128.7 (Ar), 127.4 (Ar), 127.3 (Ar), 38.8 (CH_2), 38.0 (Me*C*), 36.9 (CH_3), 22.5 (d, $J_{PC} = 10$ Hz, o-CH_3), 21.0 (p-CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.8 (d, $^2J_{PP} = 11$ Hz), −96.2 (quart, $^2J_{PP} = 11$ Hz). ^{31}P NMR (C_6D_6): δ 9.8 (broad), −96.2 (broad t, $^1J_{PH} = 281$ Hz).

[Cu(triphos)PH$_2$Mes]PF$_6$ (7). To a pink solution of $[Cu(PH_2Mes)_4]PF_6$ (40 mg, 0.05 mmol) in THF (2 mL) was added a solution of triphos (31 mg, 0.05 mmol) in THF (2 mL), and the resulting mixture was stirred for 30 min. Addition of petroleum ether (8 mL) precipitated an off-white solid. The solvent was decanted, and the solid was dried in vacuo to give 33 mg (67% yield) of the product. Anal. Calcd for $C_{50}H_{52}CuF_6P_5$: C, 60.94; H, 5.33. Found: C, 61.14; H, 5.53. IR: 3053, 2920, 2346, 1604, 1482, 1435 (vs), 1381, 1095 (s), 1026, 1000, 839 (vs), 738 (s), 695 (vs), 557 (s), 515 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.23 (5H, m, Ar), 7.04 (27H, m, Ar), 5.69 (2H, d quart, $^1J_{PH} = 317$ Hz, $^3J_{PH} = 9$ Hz, PH_2), 2.54 (6H, broad, CH_2), 2.43 (6H, o-CH_3), 2.38 (3H, p-CH_3), 1.69 (3H, broad m, CH_3). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 141.0 (Ar), 140.9 (Ar), 135.0 (m, Ar), 132.6 (m, Ar), 130.9 (Ar), 130.5 (d, $J_{PC} = 6$ Hz, Ar), 129.6 (m, Ar), 38.3 (m, CH_3), 36.6 (Me*C*), 36.1 (broad, CH_2), 23.0 (d, $J_{PC} = 10$ Hz, o-CH_3), 20.8 (p-CH_3). The expected eighth Ar peak was not observed for complexes **7** and **8**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) (40° to −30 °C): δ −18.0 (broad), −122.0 (broad), −141.1 (septet, $^1J_{PF} = 711$ Hz).

[Ag(triphos)PH$_2$Mes]BF$_4$ (8). To a pale-yellow solution of $[Ag(PH_2Mes)_4]BF_4$ (100 mg, 0.12 mmol) in THF (5 mL) was added a solution of triphos (76 mg, 0.12 mmol) in THF (4 mL). A white solid was precipitated by addition of petroleum ether to give 90 mg (75% yield) of the spectroscopically pure product. The complex decomposes in polar solvents (CH_2Cl_2, CH_3NO_2) to $Ag(triphos)BF_4$ (**10**) and L over a period of days and therefore was not obtained analytically pure by recrystallization. This decomposition occasionally caused difficulties in the NMR analysis, because the liberated PH_2Mes exchanged with the coordinated L, causing changes in the chemical shift and the J_{PH} of the PH protons in the ^1H NMR spectrum and of coordinated L in the ^{31}P NMR spectrum. Anal. Calcd for $C_{50}H_{52}AgBF_4P_4$: C, 61.81; H, 5.41. Found: C, 62.65; H, 5.42. IR: 3062, 2958, 2347, 1604, 1482, 1435 (vs), 1378, 1058 (broad, vs), 999, 826 (s), 743 (vs), 696 (vs), 514 (vs) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 7.24 (5H, m, Ar), 7.1 (25H, m, Ar), 6.96 (4H, Ar), 4.70 (4H, d, broad, $^1J_{P-H} = 280$ Hz, PH_2), 2.48 (6H, CH_2), 2.37 (12H, o-CH_3), 2.31 (6H, p-CH_3), 1.55 (3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 140.5 (Ar), 140.4 (Ar), 139.1 (Ar), 133.9 (m, Ar), 132.3 (m, Ar), 130.6 (Ar), 129.3 (broad, Ar), 38.7 (Me*C*), 37.2 (CH_2), 36.8 (CH_3), 22.9 (d, $J_{PC} = 11$ Hz, o-CH_3), 21.1 (p-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −15.3 (d, $^1J_{AgP} = 197$ Hz), −133.7 (broad). ^{31}P NMR (CD_2Cl_2): δ −15.3 (d, $^1J_{AgP} = 197$ Hz), −133.7 (broad t).

[Pd(tetraphos)PH$_2$Mes][BF$_4$]$_2$ (9). To a pale-yellow solution of $[Pd(PH_2Mes)_4][BF_4]_2$ (100 mg, 0.011 mmol) in CH_2Cl_2 (3 mL) was added a solution of tetraphos (76 mg, 0.011 mmol) in CH_2Cl_2 (3 mL) to afford a red solution, from which an orange solid was precipitated by addition of diethyl ether (15 mL). The solid was filtered and dried in vacuo to give 75 mg (30% yield) of the pure product.

Alternatively, a solution of tetraphos (226 mg, 0.34 mmol) in CH_2Cl_2 (3 mL) was mixed with a gray slurry of $[Pd(NCMe)_4][BF_4]_2$ (150 mg, 0.34 mmol) in CH_2Cl_2 (4 mL) to afford a pale yellow-green slurry, to which PH_2Mes (51 mg, 0.34 mmol) was added to give a red solution. The solution was filtered, and an orange voluminous solid was precipitated by addition of diethyl ether (15 mL). The solvent was decanted, and the solid was washed with diethyl ether (15 mL) and dried in vacuo to give 260 mg (70% yield) of analytically pure **9**.

Anal. Calcd for $C_{51}H_{55}B_2F_8P_5Pd$: C, 55.50; H, 5.04. Found: C, 55.39; H, 5.03. IR: 3052, 2917, 2301, 1604, 1571, 1482, 1435 (vs), 1306, 1280, 1061 (broad, vs), 998 (s), 888, 852, 828, 806, 744 (vs), 724 (s), 698 (vs), 520 (vs), 484 (s) cm^{-1}. ^1H NMR (CD_3NO_2): δ 7.62 (5H, m, Ar), 7.41 (12H, m, Ar), 7.21 (13H, m, Ar), 6.9 (2H, d, $J_{PH} = 4$ Hz, Ar), 5.64 (dm, $^1J_{PH} = 381$ Hz, PH_2), 3.10 (4H, br, CH_2), 3.00−2.8 (8H, br, CH_2), 2.31 (3H, p-CH_3), 1.74 (6H, o-CH_3). $^{13}C\{^1H\}$ NMR (CD_3NO_2): δ 144.7 (Ar), 143.1 (d, $J_{PC} = 9$ Hz, Ar), 135.4 (m, Ar), 134.2 (m, Ar), 133.6 (m, Ar), 133.4 (Ar), 132.1−131.6 (m, Ar), 131.1 (m, Ar), 31.1 (m, CH_2), 27.6 (m, CH_2), 23.5 (d, $J_{PC} = 10$ Hz, o-CH_3), 21.3 (p-CH_3). $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ 160.2 (d, $^2J_{PPtrans} = 323$ Hz), 47.3 (d, $^2J_{PPcis} = 38$ Hz), −94.5 (d quart, $^2J_{PPtrans} = 323$ Hz, $^2J_{PPcis} = 38$ Hz).

Ag(triphos)BF$_4$ (10). To a slurry of $AgBF_4$ (40 mg, 0.2 mmol) in THF (4 mL) was added a solution of triphos (128 mg, 0.2 mmol) in 4 mL of 1:1 THF/CH_3NO_2 to afford a pale-yellow solution. The solvent was removed, and the residue was washed with Et_2O (2 × 10 mL) to give 140 mg (83% yield) of a pale-yellow solid, which was recrystallized from CH_3NO_2/Et_2O for analysis. Anal. Calcd for $C_{41}H_{39}AgBF_4P_3$: C, 60.09; H, 4.81. Found: C, 59.86; H, 4.65. IR: 3054 (s), 2957, 1586, 1554 (s), 1483 (s), 1435 (vs), 1400, 1376, 1308, 1281, 1189, 1060 (broad, vs), 998 (vs), 850, 740 (vs), 694 (vs), 655, 512 (vs), 476 cm^{-1}. ^1H NMR (CD_3NO_2): δ 7.53−6.80 (30H, m, Ar), 2.78 (3H, CH_3), 2.08 (6H, CH_2). $^{31}P\{^1H\}$ NMR (CD_3NO_2): δ −0.3 [d, $^1J_{^{107}AgP} = 511$ Hz, $^1J_{^{109}AgP} = 591$ Hz].

H$_3$B·PH$_2$Mes (11). To PH_2Mes (500 mg, 3.3 mmol) was added $BH_3 \cdot THF$ (4 mL of a 1 M THF solution, 4 mmol). After 1 h, the solvent was pumped off and the white residue was recrystallized from THF/petroleum ether to give a white solid, 456 mg (83% yield). An analytical sample (colorless needles, mp 83 °C) was obtained by another recrystallization from ether/petroleum ether. Anal. Calcd for $C_9H_{16}BP$: C, 65.10; H, 9.73. Found: C, 65.32; H, 9.95. IR: 2978, 2937, 2918, 2866, 2739, 2556, 2392 (vs and broad), 2246, 1786, 1746, 1603, 1560, 1448, 1416, 1381, 1296, 1161, 1128, 1095, 1055, 1030, 956, 944, 901, 855, 742, 685, 630, 574, 553, 542, 530 cm^{-1}. ^1H NMR (C_6D_6): δ 6.51 (d, $J = 3$ Hz, 2H, Ar); 4.81 (d quartets, $J_{PH} = 370$ Hz, $J_{BH} = 7.8$ Hz, 2H, PH_2); 2.07 (6H, o-Me); 1.97 (3H, p-Me). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −68.8 (broad d, $J = 32$ Hz). ^{31}P NMR (C_6D_6): δ −68.8 (broad t, $J_{PH} = 370$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 141.3 (d, $J = 7.7$ Hz, quaternary Ar), 137.5 (d, $J = 108.5$ Hz, quaternary Ar), 129.9 (d, $J = 8.3$ Hz, m-Ar), 118.1 (d, $J = 57.3$ Hz, quaternary Ar), 21.8 (d, $J = 8.8$ Hz, o-Me), 21.4 (p-Me).

Crystallographic Studies. Crystal, data collection, and refinement parameters are given in Table 2. The systematic absences in the data for **1** and **7·solvent** are uniquely consistent for the reported space groups. No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data for **3** and **6**. Solution in $P\bar{1}$ yielded chemically reasonable and computationally stable results. For **1**, all inspected crystals were either twinned or multiple. Approximately 5% of the data were rejected because of asymmetrical profiles caused by diffraction contributions from a minor twin or satellite crystal.

The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. No absorption corrections were necessary because of the <10% variation of the azimuthal scans. To conserve data in **1**, phenyl carbon atoms were isotropically refined as part of rigid bodies. Attempts to model two residual peaks in the difference map of **7·solvent**, which were located near an inversion center and away from the compound molecule, as a chemically recognizable solvent were unsuccessful; they were assigned carbon atom identities and refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions except those for the apparent solvent molecule in **7·solvent** which were ignored.

All software and sources of the scattering factors are contained in either the SHELXTL (5.3) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI).

Addition of PH_2Mes to Complexes 1−9. The general procedure follows that described here for **2**. PH_2Mes (14 mg, 0.092 mmol) was added to a solution of **2** (20 mg, 0.023 mmol) in CH_2Cl_2 (1.5 mL), and the reaction was monitored by $^{31}P\{^1H\}$ NMR. Exchange in Pd complexes **2** and **9** was also monitored similarly in nitromethane.

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Supporting Information Available: Tables of bond lengths, bond angles, atomic coordinates and equivalent isotropic displacement coefficients, and H-atom coordinates and isotropic displacement coefficients for **1**, **3**, **6**, and **7·solvent** (28 pages). Four X-ray crystallographic files, in CIF format, are available. Access and ordering information is given on any current masthead page.

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