Synthesis and Coordinating Properties of Heterocyclic-Substituted Tertiary Phosphines[1]

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Tris(thiazol-2-yl)phosphine, **2**, has been prepared by reaction of the corresponding heteroaryl organolithium reagent and PCl_3. Attempts to prepare other heteroaryl-substituted phosphines, such as tris(benzothiazol-2-yl)- (**3**) and tris(1-methylimidazol-2-yl)phosphines (**6**), using this procedure, were unsuccessful. Heteroaryltrimethylsilanes, readily accessible from the reaction between a heteroaryl organometallic reagent and chlorotrimethylsilane (CH_3SiCl), afford the desired heteroaryl-substituted phosphines when treated with PCl_3. The heteroaryl–silicon bonds of these silanes also undergo facile electrophilic cleavage by $(C_6H_5)PCl_2$ and $(C_6H_5)_2PCl$ and yield the unsymmetrically substituted phosphines. The phosphines obtained in this work react readily with (1,5-cyclooctadiene)dimethylplatinum(II) and generate *cis*-dimethylbis(phosphine)platinum(II) complexes in which the potentially multidentate ligands are exclusively monodentate. The coordinated phosphines are bound to platinum through the phosphorus atom of the ligand.

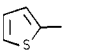
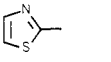
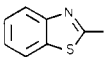
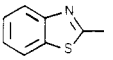
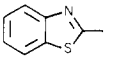
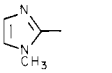
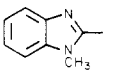
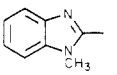
Introduction

Intramolecular cyclometalation reactions, involving insertion of a transition metal into a carbon–hydrogen bond of a coordinated ligand, are common reactions among transition-metal complexes.[3] Suppression of these reactions would be useful in studying intermolecular carbon–hydrogen bond activation by homogeneous transition-metal complexes. We describe here the syntheses of a series of heteroaryl-substituted tertiary phosphines which cannot undergo cyclometalation when coordinated to a transition-metal center. We also hoped that such phosphines might provide access to water-soluble transition-metal complexes, a class of compounds whose chemistry has recently received considerable attention.[4,5] In fact, within the scope of our studies these heteroaromatic phosphines show neither the properties required for high-temperature homogeneous organometallic chemistry nor for the synthesis of water-soluble transition-metal complexes. They are nonetheless new ligands with unexplored properties, and we report their syntheses here.

A number of simple heterocyclic-substituted phosphines have been previously reported.[6] The heterocyclic substituents have generally been those containing a single heteroatom (e.g., furan, thiophene, and pyridine), although recently Curtis and Brown[7] have reported the syntheses of tris(1*H*-imidazol-2-yl) phosphine[8] and two of its 4,5-dialkyl-substituted analogues.

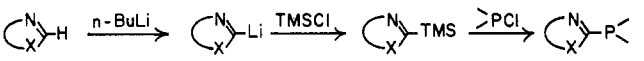
Most heterocyclic-substituted phosphines (e.g., tris(2-thienyl)phosphine, **1**) have been prepared by nucleophilic displacement on a phosphorous trihalide by an appropriate organometallic reagent.[6,9] We have prepared **1** and **2** in such fashion.[6] Metal–halogen exchange between 2-bromothiazole and *n*-butyllithium in ether (−78 °C), or direct deprotonation of thiazole by *n*-butyllithium, afforded a homogeneous solution of 2-lithiothiazole (stable

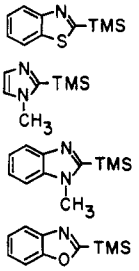
Table I. Heteroaromatic-Substituted Phosphines, $R^1R^2R^3P$

compd	substituents	method (% yield)
1	R^1, R^2, R^3 = 	A (78, 70[b])
2	R^1, R^2, R^3 = 	A (47,[c] 64[d])
3	R^1, R^2, R^3 = 	B (83)
4	$R^1 = C_6H_5$; R^2, R^3 = 	B (77)
5	$R^1, R^2 = C_6H_5$; R^3 = 	B (76)
6	R^1, R^2, R^3 = 	B (66)
7	$R^1, R^2 = C_6H_5$; R^3 = 	B (62)
8	$R^1 = C_6H_5$; R^2, R^3 = 	B (47)

[a] Method A involved reaction between a heteroaryl organolithium reagent and phosphorous trichloride; method B involved the reaction between a 2-(trimethylsilyl)-substituted heteroaromatic and a phosphorous(III) halide. [b] From ref 9. [c] The requisite organolithium reagent was prepared by metal-halogen exchange between 2-bromothiazole and *n*-BuLi. [d] 2-Lithiothiazole was prepared by metalation of thiazole with *n*-BuLi.

Scheme I. Synthesis of Heteroaromatic Phosphines





(1) Supported by the National Science Foundation, Grant 8012722 CHE.

(2) NIH Postdoctoral Fellow, 1979–1981, 1F32 CA 06462-01.

(3) Bruce, M. I. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 73–86. Dehand, J.; Pfefer, M. *Coord. Chem. Rev.* **1976**, *18*, 327–52. Omae, I. *Ibid.* **1980**, *32*, 235–71.

(4) Joo, F.; Toth, Z. *J. Mol. Catal.* **1980**, *8*, 369–83 and references cited therein.

(5) Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 306–7. Wilson, M. E.; Nuzzo, R. G.; Whitesides, G. M. *Ibid.* **1978**, *100*, 2269–70.

(6) Redmore, D. *Chem. Rev.* **1971**, *71*, 315–37.

(7) Curtis, N. J.; Brown, R. S. *J. Org. Chem.*, **1980**, *45*, 4038–40.

(8) Although *Chemical Abstracts* cites this compound as 2,2′,2″-phosphinidynetris-1*H*-imidazole, we have chosen to refer to the phosphines described here using a semitrivial system of nomenclature in which the heterocyclic moiety is viewed as a substituent on phosphine, PH_3, rather than the reverse.

(9) Isslieb, K.; Brack, A. *Z. Anorg. Allg. Chem.* **1957**, *292*, 245–53.

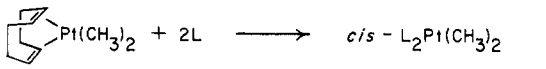
0022-3263/82/1947-1489$01.25/0

below −60 °C).[10,11] A solution of PCl_3 in ether was added to the solution of 2-lithiothiazole. After several hours at −60 °C the reaction mixture was quenched with aqueous NH_4Cl. Rapid workup, particularly important for the reaction mixture resulting from metal–halogen exchange between 2-bromothiazole and *n*-BuLi, cleanly afforded the desired phosphine. Attempts to extend this procedure to the syntheses of **3** and **6** were unsuccessful even though the requisite organometallic reagents were readily accessible.[12]

An alternate synthetic strategy, applicable to most of the phosphines listed in Table I, was developed. This approach, outlined in Scheme I, involves electrophilic cleavage of the C–Si bond of a 2-(trimethylsilyl)-substituted heteroaromatic compound.[13,14] Extensive studies of such heterocyclic-substituted silanes have established that they are susceptible to facile electrophilic cleavage of the C–Si bond.[15–17] For example, silane **9** reacts with benzoyl chloride to give 2-benzoylbenzothiazole (81%) and Me_3SiCl. The present study illustrates that phosphorous halides (specifically PCl_3, $(C_6H_5)PCl_2$, $(C_6H_5)_2PCl$, and $POCl_3$[18]) are also reactive toward (benzothiazol-2-yl)-, (1-methylimidazol-2-yl)-, and (1-methylbenzimidazol-2-yl)-trimethylsilanes, **9**–**11**, respectively, and afford the phosphines listed in Table I in moderate to good yields.

Reaction between **9** and neat PCl_3 yielded, after removal of Me_3SiCl by distillation, a solid residue which, after recrystallization, gave analytically pure **3** (83%). Unsymmetrically substituted tertiary phosphines are also accessible by this method. Treatment of silane **9** with $(C_6H_5)PCl_2$ afforded **4** (77%) and treatment of **9** with $(C_6H_5)_2PCl$ gave **5** (76%). Both (1-methylimidazol-2-yl)- and (1-methylbenzimidazol-2-yl)trimethylsilanes are more reactive toward the phosphorous halides than is silane **9**. Reaction between **10** and PCl_3 affords phosphine **6** (66%) after purification. Although silane **11** afforded phosphines **7** (47%) and **8** (62%) upon treatment with $(C_6H_5)PCl_2$ and $(C_6H_5)_2PCl$, respectively, it yielded only an intractable mixture of products when treated with PCl_3. Metalation of benzoxazole with *n*-BuLi, followed by treatment with Me_3SiCl, afforded a compound tentatively identified as (benzoxazol-2-yl)trimethylsilane, **12** (49%).[19] Treatment of the highly unstable silane **12** with PCl_3, although producing nearly the stoichiometric amount of Me_3SiCl, afforded a highly colored, inseparable mixture of products. The reactivity of **12** was not examined further.

Scheme II. Synthesis of Dimethylplatinum(II) Complexes of Heteroaromatic Phosphines



Complex	Ligand (L)
13	1
14	2
15	3
16	6

The phosphines listed in Table I are soluble in most organic solvents. Phosphine **6** also exhibits an appreciable solubility in water, perhaps accounting for our inability to isolate **6** from the reaction between 2-lithio-1-methylimidazole and PCl_3. The nucleophilic reactivity of phosphine **2** toward iodomethane was briefly studied. Whereas tris(2-thienyl)phosphine reacted readily with iodomethane and afforded the corresponding phosphonium salt (85%),[20] phosphine **2** reacted slowly, apparently as an ambident nucleophile, and afforded a mixture of products as determined by ^{31}P NMR. Attempted oxidation of phosphine **2** with 30% H_2O_2 afforded none of the desired phosphine oxide, possibly as a consequence of hydrolysis to the corresponding phosphinic acid, a reaction noted to be quite facile for other heteroaryl-substituted phosphine oxides.[20]

In summary, the synthetic method reported here afforded mono-, di-, and triheteroaryl-substituted tertiary phosphines in several cases where the direct electrophilic reaction of a phosphorous halide with a heteroaryl organometallic reagent was unsuccessful. The procedure involves the electrophilic cleavage of the C–Si bond of a heteroaryltrimethylsilane and the formation of a C–P bond in its place. The reactions are conducted in the absence of solvent, often only requiring recrystallization of the crude reaction mixture to afford the analytically pure phosphine. The phosphines, contrary to a suggestion in the literature,[21] appear to be quite air-stable, even at room temperature. Difficulties experienced in handling other heteroaryl-substituted phosphines may be due, at least in part, to reactive byproducts carried through the workup procedure. Such problems are avoided in the present method since the principal byproduct, Me_3SiCl, is removed by distillation as it is formed. The procedure represents a useful addition to other synthetic approaches currently in use.

Preparation of Dimethylbis(phosphine)platinum(II) Complexes. Treatment of a solution of (1,5-cyclooctadiene)dimethylplatinum(II), $(COD)Pt(CH_3)_2$, in ether with phosphines **1**–**3** and **6** afforded the respective bis(phosphine) complexes in good yields (Scheme II).[22] Even phosphine **6**, which is presumably quite sterically hindered by virtue of its three NCH_3 groups, reacts readily with $(COD)Pt(CH_3)_2$ at 0 °C. By comparison, tris(2-methylphenyl)phosphine does not react with $(COD)Pt(CH_3)_2$

(10) Roussel, P.; Metzger, J. *Bull. Soc. Chim. Fr.* **1962**, *2075*–8. Eyles, C. T.; Sykes, P.; Downes, J. E. *J. Chem. Soc.* **1965**, 4265–71.

(11) Beraud, J.; Metzger, J. *Bull. Soc. Chim. Fr.*, **1962**, 2072–4. Braun, J. A.; Metzger, J. *Ibid.*, **1967**, 503–10. Breslow, R.; McNelis, E. *J. Am. Chem. Soc.* **1959**, *81*, 3080–2.

(12) Mallan, J. M.; Bebb, R. L. *Chem. Rev.* **1969**, *69*, 693–755.

(13) Eaborn, C. *J. Organomet Chem.* **1975**, *100*, 43–57. Boe, B. *Ibid.*, **1976**, *107*, 139–217.

(14) Treatment of trichlorophenylsilane with PCl_3 and $AlCl_3$ affords dichlorophenylphosphine and tetrachlorosilane in a reaction which resembles that reported herein; Yakubovich, A. Ya.; Motsarev, G. V. *Zh. Obshch. Khim.* **1953**, *23*, 771–6; **1953**, *23*, 1547–52; *Dokl. Akad. Nauk. S.S.S.R.* **1953**, *88*, 87–9.

(15) Pinkerton, F. H.; Thames, S. F. *J. Heterocycl. Chem.* **1971**, *8*, 257–9. Jutzi, P.; Hoffman, H.-J. *J. Organomet. Chem.* **1972**, *40*, C61–C63; *Chem. Ber.* **1973**, *106*, 594–605. Jutzi, P.; Hoffman, H.-J.; Wyes, K.-H. *J. Organomet. Chem.* **1974**, *81*, 341–350. Jutzi, P.; Hoffman, H.-J.; Beier, K.; Wyes, K.-H. *Ibid.* **1974**, *82*, 209–216.

(16) Jutzi, P.; Sakriss, W. *Chem. Ber.* **1973**, *106*, 2815–24. Pinkerton, F. H.; Thames, S. F. *J. Heterocycl. Chem.* **1972**, *9*, 67–72.

(17) Pinkerton, F. H.; Thames, S. F. *J. Heterocycl. Chem.* **1969**, *6*, 433; *J. Organomet. Chem.* **1970**, *24*, 623–7. Jutzi, P.; Lorey, O. *Ibid.* **1976**, *104*, 153–60.

(18) Treatment of **9** with $POCl_3$ afforded nearly the stoichiometric amount of Me_3SiCl upon distillation. The ^{31}P NMR spectrum of the crude mixture displayed a signal at δ 3.2 and two minor (<5% of the signal at δ 3.2) signals at δ 16.8 and −22.6 (the ^{31}P NMR spectrum of **9** displayed a signal at δ −20.8 under similar conditions). The ^1H NMR spectrum of the crude product resembled that of phosphine **3**. A pure sample of the desired phosphine oxide could not be obtained, perhaps as a result of its hydrolytic instability (cf. ref 17).

(19) A compound tentatively identified as (benzoxazol-2-yl)trimethylsilane, **12**, was isolated in 49% yield from the reaction between 2-lithiobenzoxazole and Me_3SiCl: bp 93–95 °C (6 torr); ^1H NMR (60 MHz, $CDCl_3$) δ 0.33 (s, 9 H, $Si(CH_3)_3$), 6.80–7.53 (m, 4 H).

(20) Allen, D. W.; Hutley, B. G.; Mellor, M. T. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1705–8. Allen, D. W.; Hutley, B. G.; Mellor, M. T. J. *Ibid.* **1972**, 63–67; and other papers in this series.

(21) Newkome, G. R.; Hager, D. C. *J. Org. Chem.* **1978**, *43*, 947–9.

(22) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411–28 McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–8.

under similar conditions. In refluxing benzene or toluene, reaction of tris(2-methylphenyl)phosphine with (COD)-$Pt(CH_3)_2$ yielded a mixture of cyclometalated products (by ^1H and ^{31}P NMR).[23-25] The greater reactivity of **6**, compared to that of tris(2-methylphenyl)phosphine, probably reflects a decrease in the steric requirement of the ligand (Tolman[26] estimates a cone angle of 194 ± 6° for tris(2-methylphenyl)phosphine) and an increase in electron density on the phosphorus atom of **6** (vide infra).

The structures of the platinum complexes were established by ^{31}P $\{^1H\}$ NMR, ^1H NMR, and microanalysis. Although the phosphines are potentially multidentate ligands, the spectral characteristics of the complexes **13–16** suggest that the ligands are exclusively monodentate, bonded to platinum through the phosphorus atom of the ligand. The ^{31}P spectra of complexes **13–16** display characteristic 1:4:1 triplets for the coordinated phosphines at δ −3.4 (J_{PtP} = 1820 Hz), 6.2 (J_{PtP} = 1802 Hz), 13.2 (J_{PtP} = 1782 Hz), −13.9 (J_{PtP} = 1857 Hz), respectively. The magnitude of the observed ^{195}Pt–^{31}P coupling constants are consistent with the expected cis geometry of the complexes.[22,27,28]

The ^1H NMR spectra of the complexes **13–16** are also in accord with the proposed structures. Integration of these spectra reveals that that the phosphine ligands and the methyl substituents on platinum are present in a 1:1 molar ratio. The ^1H NMR spectra of **13–15** are otherwise unexceptional. The ^1H NMR spectrum of **16** suggests that the phosphines present in the complex experience some hindrance to free rotation. At 24 °C (ambient probe temperature) the ^1H NMR spectrum of **16** (Me_2SO-d_6) reveals a very broad signal at δ 3.30 ($w_{1/2}$ = 47 Hz) due to the NCH_3 groups on the coordinated ligand. At 77 °C this signal becomes much sharper ($w_{1/2}$ = 4 Hz) and new peaks appear which do not coalesce upon cooling. The ^1H and ^{31}P NMR spectra of a sample of **16** which had been heated to 75 °C and then allowed to cool to ambient temperature displayed signals due to **16**, dissociated phosphine **6**, and a new phosphine–platinum complex (^{31}P NMR δ −11.0 (J_{PtP} = 1877 Hz)). Upon prolonged heating at 75 °C the intensities of the signals due to **16** and the other platinum-containing complex decreased in intensity, while the intensity of the signal due to free phosphine **6** increased. This observation suggests that the second phosphine–platinum complex in the mixture may be the result of phosphine dissociation from **16** and subsequent binding of Me_2SO to the coordinatively unsaturated platinum intermediate.

Bis(phosphine) complexes **13–16** are soluble in polar organic solvents such as pyridine, Me_2SO, and CH_2Cl_2 and are virtually insoluble in solvents such as benzene and cyclohexane. All of the complexes are also insoluble in water. Even complex **16**, bearing water-soluble phosphine **6**, is insoluble in water.

The thermolytic behavior of platinum **13–16** has been briefly studied. The solubility properties of the complexes required that such studies be conducted in pyridine, Me_2SO, or CH_2Cl_2. Chlorinated solvents, such as CH_2Cl_2, are inappropriate for studying the thermolyses of the platinum complexes since platinum(II) readily inserts into C–Cl bonds.[29] Thermolyses of **13–16** in pyridine, or Me_2SO, resulted in dissociation of the coordinated phosphines and formation of intractable platinum-containing deposits.[30] Only unreacted starting material and dissociated phosphine could be detected by ^{31}P NMR of the thermolysis mixtures. Although a more detailed analysis of these mixtures is complicated by the presence of deposited platinum metal, it is clear from the ^{31}P NMR spectra of the mixtures that cyclometalation between a coordinated phosphine and platinum did not occur.

A variety of transition-metal compelxes have been reported in which a heteroaryl-substituted phosphine, such as tris(2-pyridyl)phosphine **17**, serves as a multidentate ligand.[31] Studies by Balch and co-workers further show that phosphine **17** can serve as a bridging ligand, providing access to binuclear complexes.[32] We have been unable to detect a chelated (or phosphine bridged) complex in the reaction mixture between $(COD)Pt(CH_3)_2$ and the phosphines described here. Only complex **14** could be detected by ^{31}P NMR of the mixture resulting from reaction between $(COD)Pt(CH_3)_2$ and 1 molar equiv of phosphine **2**; a chelated (or bridged) complex, if formed as an intermediate, is much more reactive than $(COD)Pt(CH_3)_2$ toward free phosphine. Ang and co-workers have noted that diphenyl(2-pyridyl)phosphine serves as a monodentate ligand toward platinum, binding to the metal exclusively through the phosphorus atom of the ligand.[33] Phosphine

(23) Heating a solution of 1.0 mmol of tris(2-methylphenyl)phosphine and 0.5 mmol of $(COD)Pt(CH_3)_2$ in refluxing benzene (or toluene) afforded a mixture of two products identified as *cis*-$Pt(CH_3)(CH_2C_6H_4PAr_2)(PAr_3)$ [**18**; ^{31}P NMR (C_6H_6) δ 23.0 (1:4:1 t, J_{PtP} = 1920 Hz), 33.9 (1:4:1 t, J_{PtP} = 1899 Hz; ^1H NMR (250 MHz, C_6D_6) δ 0.88 (1:4:1 t of m, 3H, $PtCH_3$, J_{PtH} = 68.4 Hz), 1.47, 1.52, 1.77, 2.21, 2.86 (br s, 3 H, $ArCH_3$), 4.05 (complex m, 2 H, $PtCH_2$), 6.30–7.55 (m, 23 H, ArH), 8.95 (br s, 1 H, ArH)] and *trans*-$(Ar_2PC_6H_4CH_2)_2Pt$ [**19**; ^{31}P NMR (C_6H_6) δ 31.0 (1:4:1 t, J_{PtP} = 3020 Hz)]. Platinum complex **18** was isolated pure from the reaction mixture following preparative TLC (1000 μm of silica gel, Analtech, 10% (v/v) CH_2Cl_2/pentane elution). Although **18** was stable at 78 °C in benzene, at 138 °C it underwent thermolysis, affording **19** as the major component in a mixture of products. A platinum complex very similar to **18**, $Pt(CH_3)(CH_2C_6H_4PAr\text{-}t\text{-}Bu)(PAr_2\text{-}t\text{-}Bu)$, has been reported and undergoes thermolysis at 135 °C in xylene, affording *trans*-$(t\text{-}BuArPC_6H_4CH_2)_2Pt$, an analogue of **19**. (Ar = 2-$CH_3C_6H_4$).[24]

(24) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 754–63. Cheney, A. J.; McDonald, W. S. O'Flynn, K.; Shaw, B. L.; Turtle, B. L. *Chem. Commun.* **1973**, *128*–9.

(25) *trans*-$PtI_2[(2\text{-}CH_3C_6H_4)_3P]_2$ has been reported to be resistant to cyclometalation even under forcing conditions (cf. ref 21). Alyea, E. C.; Dias, S. A.; Ferguson, G.; Roberts, P. J. *J. Chem. Soc., Dalton Trans.* **1979**, 948–51.

(26) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–48.

(27) The ^{195}Pt–^{31}P coupling constants for *cis*-dimethylbis(phosphine)platinum(II) complexes typically range between 1750 and 1900 Hz; for example, *cis*-$[(C_6H_5)_3P]_2Pt(CH_3)_2$, J_{PtP} = 1899 Hz (Eaborn, C.; Odell, K. J.; Pidcock, A. *J. Chem. Soc., Dalton Trans.* **1979**, 758–60); *cis*-$[(CH_3)_3P]_2Pt(CH_3)_2$, J_{PtP} = 1790 Hz (Goodfellow, R. J.; Hardy, M. J.; Taylor, B. F. *Ibid.* **1973**, 2450–3); $(C_6H_5)_2P(CH_2)_n(C_6H_5)_2PPt(CH_3)_2$ (n = 3), J_{PtP} = 1790 Hz, n = 2, J_{PtP} = 1794 Hz (Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *Ibid.* **1976**, 439–46); *cis*-$[(C_6H_5)P(CH_3)_2]_2Pt(CH_3)_2$, J_{PtP} = 1819 Hz (Cheney, A. J.; Mann, B. E.; Shaw, B. L. *Chem. Commun.* **1971**, 431); and *cis*-$[(C_2H_5)_3P]_2Pt(CH_3)_2$, J_{PtP} = 1780 Hz (Allen, F. H.; Pidcock, A. *J. Chem. Soc. A* **1968**, 2700–4).

(28) The ^{195}Pt–^{31}P coupling constants for *trans*-dialkyl- and *trans*-diarylbis(phosphine)platinum(II) complexes are typically much larger than those for the corresponding cis complexes; eg., *trans*-$[(2\text{-}C_3H_7)_3P]_2Pt(CH_3)_2$, J_{PtP} = 2943 Hz, *cis*-$[(2\text{-}C_3H_7)_3P]_2Pt(CH_3)_2$, J_{PtP} = 1825 Hz (DiCosimo, R.; Whitesides, G. M., unpublished results); *trans*-$[(C_2H_5)_3P]_2Pt(C_6H_5)_2$, J_{PtP} = 2824 Hz, *cis*-$[(C_2H_5)_3P]_2Pt(C_6H_5)_2$, J_{PtP} = 1704 Hz (Heaton, B. T.; Pidcock, A. *J. Organomet. Chem.* **1968**, *14*, 253–7. Pregosin, P. S.; Kunz, R. W. In "NMR Basic Principles and Progress"; Diehl, P.; Fluck, E.; Kosfeld, R., Ed.; Springer-Verlag: New York, 1979; Vol. 16).

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1 binds to Ni(II) exclusively through the phosphorus atom of the ligand and is apparently a better ligand toward the metal than is triphenylphosphine, 17.[34] The enhanced donor ability of 1 relative to 17 reflects favorable p_π–d_π interactions between the thienyl substituents and the phosphorus atom of 1. It is possible that similar p_π–d_π interactions between the 1-methylimidazole substituents and the phosphorus atom of 6 may account for its increased reactivity toward $(COD)Pt(CH_3)_2$, relative to tris(2-methylphenyl)phosphine.[35]

Conclusion

Mono-, di-, and triheteroaryl-substituted phosphines whose syntheses would otherwise be difficult can be prepared by reaction of a phosphorous(III) halide and a trimethylsilyl-substituted heteroaromatic. The ready availability of these heteroaromatic silanes makes this synthetic method a useful and convenient one.[36] The phosphines obtained by this approach react readily with $(COD)Pt(CH_3)_2$, affording the *cis*-dimethylbis(phosphine)platinum(II) complexes. In these complexes the potentially multidentate ligands are exclusively monodentate, binding to platinum through the phosphorus atom of the ligands.

Experimental Section

General Procedures. All manipulations of air-sensitive organometallic reagents were conducted by use of standard bench-top techniques.[37] The phosphorous halides (PCl_3, $(C_6H_5)PCl_2$, and $(C_6H_5)_2PCl$) and chlorotrimethylsilane were distilled immediately prior to use. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone dianion. Solutions of *n*-butyllithium in ether were prepared and standardized according to Gilman.[38] Compounds used in this work which were prepared according to literature procedures include thiazole,[11] 2-bromothiazole,[11] tris(2-thienyl)phosphine,[9] (benzothiazol-2-yl)-,[15] (1-methylimidazol-2-yl)-,[16] and (1-methylbenzimidazol-2-yl)trimethylsilane.[16] All other chemicals were reagent grade and used without further purification unless otherwise specified. Melting points were measured with sealed capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Proton NMR spectra were recorded on a Varian Model T-60 (60 MHz) or on a Bruker WM-250 (250 MHz) nuclear magnetic resonance spectrometer. Proton-decoupled ^{31}P NMR spectra were recorded on a modified Bruker HFX-90 (36.4 MHz), a JEOL FX-90Q (36.3 MHz), or a Bruker WM-250 (101.3 MHz) spectrometer. The ^{31}P NMR chemical shifts are reported in parts per million from external 85% phosphoric acid (downfield shifts positive). Mass spectra were recorded on a Varian MAT 44 mass spectrometer operating at an ionizing voltage of 70 eV. Infrared spectra were recorded on a Perkin-Elmer Model 257 or 598 spectrometer. Microanalyses were performed by Spang Microanalytical Laboratory.

Tris(thiazol-2-yl)phosphine (2). Procedure A. To a 50-mL flask was added 20.0 mL of a 0.95 M solution of *n*-BuLi (19.2 mmol) in ether. The solution was cooled to −65 °C. To the cold solution was added 1.70 g (20 mmol) of thiazole in 5 mL of ether. The rate of addition was adjusted so that the internal temperature remained at, or below, −65 °C. Following the addition the yellow solution was stirred at −65 °C for an additional hour. To the resulting homogeneous solution was added 0.76 g (5.5 mmol) of PCl_3 in 5 mL of ether. The reaction mixture was stirred at −65 °C for 2 h and then transferred through a stainless steel cannula into 50 mL of degassed, saturated aqueous NH_4Cl. Water was added to the resulting suspension until all of the precipitated salts had dissolved. The combined organic extracts were dried over anhydrous Na_2SO_4 and filtered. Treatment of this solution with Darco, filtration through Celite, and removal of the solvent under reduced pressure afforded 0.85 g of a crystalline residue. Recrystallization of this material from a two-phase mixture of CH_3OH/*n*-hexane afforded 0.75 g (2.6 mmol) of **2**: mp 97–99 °C; ^1H NMR (60 MHz, CD_2Cl_2) δ 7.63 (d, 3 H, J = 4 Hz), 8.05 (d, 3 H, J = 4 Hz); ^{31}P NMR (CH_2Cl_2) δ −32.0; IR (KBr) 3115 (m), 1460 (m), 1360 (m), 1345 (m), 1305 (s), 1145 (s), 1035 (s), 1020 (s), 900 (m), 750 (vs), 630 (m), 620 (m), 510 (s), 440 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 283 (M^+, 13), 199 (100), 91 (22), 85 (27), 70 (53), 63 (60), 58 (78), 57 (74).

Anal. Calcd for $C_6H_6N_3PS_3$: C, 38.15; H, 2.13; P, 10.93. Found: C, 38.20; H, 2.30; P, 10.99.

Procedure B. To 20.2 mL of 0.95 M *n*-BuLi in ether, at −70 °C, was added a solution of 3.28 g (20 mmol) of 2-bromothiazole in 5 mL of ether. Treatment of the resulting solution with a solution of 0.76 g (5.5 mmol) of PCl_3 in 5 mL of ether and workup of the reaction mixture as described above (procedure A) afforded 1.35 g (4.8 mmol) of crude **2**. Recrystallization of this crude material as above gave 1.00 g (3.5 mmol) of **2** whose spectral characteristics were indistinguishable from those listed above. Rapid workup is essential with this procedure in order to avoid extensive decomposition of the reaction mixture.

Tris(benzothiazol-2-yl)phosphine (3). To a 1-mL flask was added 2.10 g (10 mmol) of silane **9** and 0.41 g (3 mmol) of PCl_3. The resulting colorless liquid was stirred at room temperature for 2 h. A short-path distillation head was attached to the reaction flask and the mixture was heated at 60 °C for 0.5 h. Distillation afforded a colorless liquid which was identified as Me_3SiCl by its ^1H NMR and IR spectra. The reaction mixture eventually solidified and was heated at 100–110 °C for 10 h and was then allowed to cool to ambient temperature. Recrystallization of the solid residue from CH_2Cl_2/*n*-pentane gave 1.1 g (2.5 mmol) of **3** as colorless needles: mp 201–202 °C; ^1H NMR (60 MHz, CD_2Cl_2) δ 7.31–7.90 (m, 6 H), 7.95–8.33 (m, 6 H); ^{31}P NMR (THF) δ −20.8; IR (KBr) 3058 (w), 1502 (s), 1412 (s), 1314 (s), 998 (s), 846 (s), 752 (s), 720 (s), 674 (s), 430 (s), 425 (s), 362 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) M^+ absent, 299 (30), 164 (14), 139 (23), 107 (20), 69 (25), 63 (100).

Anal. Calcd for $C_{21}H_{12}N_3PS_3$: C, 58.18; H, 2.79; P. 7.23. Found: C, 58.13; H, 2.89; P, 7.14.

Bis(benzothiazol-2-yl)phenylphosphine (4). Treatment of 2.00 g (9.6 mmol) of **9** with 0.86 g (4.8 mmol) of $(C_6H_5)PCl_2$ afforded a solid residue after removal of Me_3SiCl as described above for **3**. Recrystallization of the solid residue from CH_2Cl_2/CH_3OH afforded 1.38 g (3.7 mmol) of **4**: mp 127–128 °C; ^1H NMR (60 MHz, CD_2Cl_2) δ 7.23–8.27 (complex m, 13 H); ^{31}P NMR (CH_2Cl_2) δ −13.5; IR (KBr) 3055 (w), 1450 (s), 1430 (s), 1420 (s), 1408 (s), 750 (vs) cm^{-1}; mass spectrum, *m/e* (relative intensity) 376 (M^+, 6), 302 (38), 244 (36), 139 (31), 108 (38), 107 (89), 105 (31), 77 (52), 63 (100), 51 (31).

Anal. Calcd for $C_{20}H_{13}N_2PS_2$: C, 63.81; H, 3.48. Found: C, 63.84, H, 3.53.

(Benzothiazol-2-yl)diphenylphosphine (5). Similar treatment of 1.05 g (5 mmol) of **9** with 1.10 g (5 mmol) of $(C_6H_5)_2PCl$ afforded a solid residue which after flash chromatography on 30 g of silica gel (0.040–0.063 mm, Merck), using CH_2Cl_2 elution, gave 1.20 g (3.8 mmol) of **5**. Recrystallization from CH_3OH gave **5** as colorless plates: mp 87–88 °C; ^1H NMR (60 MHz, C_6D_6) δ 6.09–8.30 (complex m, 14 H); ^{31}P NMR (C_6H_6) δ −8.2; IR (KBr) 3090 (w), 1662 (w), 1498 (s), 1470 (s), 1450 (s), 1430 (s), 1330 (s), 1000 (s), 780 (s), 755 (s), 708 (s), 500 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 319 (M^+, 100), 318 (63), 243 (19), 183 (86), 108 (37), 107 (62), 77 (24), 63 (33), 62 (32), 51 (38), 50 (39).

Anal. Calcd for $C_{19}H_{14}NPS$: C, 71.46; H, 4.42. Found: C, 71.44; H, 4.38.

Tris(1-methylimidazol-2-yl)phosphine (6). Treatment of 4.50 g (29.2 mmol) of freshly distilled silane **10** with 1.33 g (9.9 mmol) of PCl_3, at 0 °C, resulted in a very exothermic reaction. Following the slow addition of PCl_3 the mixture was stirred at

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0–5 °C for 2 h and then allowed to warm to ambient temperature. The mixture was then heated at 90–95 °C for 18 h during which time nearly the stoichiometric amount of Me_3SiCl was collected by distillation. The reaction mixture was allowed to cool to ambient temperature whereupon it solidified. Trituration of the solid residue with cold (−15 °C) acetone afforded 1.8 g (6.6 mmol) of **6** as a slightly-yellow crystalline solid, which was pure by ^1H and ^{31}P NMR. Sublimation of this material (125 °C (0.005 torr)) afforded analytically pure **6**: mp 203–205 °C (subl); ^1H NMR (60 MHz, CD_2Cl_2) δ 3.40 (s, 9 H, NCH_3), 7.13 (s, 6 H); ^{31}P NMR (CH_2Cl_2) δ −60.0, (D_2O) −62.3; IR (KBr) 3115 (m), 3105 (m), 2946 (m), 1505 (m), 1448 (s), 1408 (s), 1348 (s), 1282 (s), 1116 (m), 914 (s), 864 (m), 784 (s), 778 (s), 745 (vs), 700 (s), 690 (s), 678 (s), 572 (vs), 495 (vs), 474 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 214 (M^+, 11), 193 (15), 178 (18), 125 (20), 111 (23), 95 (35), 83 (33), 70 (18), 54 (20), 42 (100).

Anal. Calcd for $C_{12}H_{15}N_6P$: C, 52.55; H, 5.51; P, 11.29. Found: C, 52.62; H, 5.60; P, 11.33.

(1-Methylbenzimidazol-2-yl)diphenylphosphine (7). To 1.66 g (8.1 mmol) of silane **11** in a 10-mL flask was added, at 0–5 °C, 1.45 mL (8.1 mmol) of $(C_6H_5)_2PCl$. The reaction mixture was allowed to warm to ambient temperature. The reaction flask was heated at 90–95 °C for 1.5 h and the Me_3SiCl produced was removed by distillation. The reaction mixture was allowed to cool to ambient temperature. Flash chromatography of the residue on 30 g of silica gel (0.040–0.063 mm, Merck), using in sequence 125 mL of CH_2Cl_2, 125 mL of 1% (v/v) CH_3OH/CH_2Cl_2, and 250 mL of 2% (v/v) CH_3OH/CH_2Cl_2, afforded (in the last 375 mL of eluent) 1.58 g (5.0 mmol) of **7** as a viscous oil which solidified upon standing. Recrystallization of the solid from CH_2Cl_2/*n*-pentane gave **7** as colorless prisms: mp 98–99.5 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 3.80 (d, 3 H, NCH_3, *J* = 0.9 Hz), 7.32–7.40 (m, 7 H), 7.47–7.54 (m, 4 H), 7.83 (m, 1 H); ^{31}P NMR ($CHCl_3$) δ −23.9; IR (KBr) 3046 (w), 2925 (s), 1586 (w), 1480 (m), 1465 (m), 1440 (s), 1415 (m), 1320 (s), 1275 (s), 1232 (m), 1090 (s), 1020 (s), 1000 (m), 808 (s), 740 (vs), 724 (s), 700 (s), 690 (s), 560 (m), 540 (m), 496 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 316 (M^+, 85), 315 (100), 238 (24), 183 (54), 107 (36), 77 (30), 51 (34).

Anal. Calcd for $C_{20}H_{17}N_2P$: C, 75.94; H, 5.42. Found: C, 75.82; H, 5.39.

Bis(1-methylbenzimidazol-2-yl)phenylphosphine (8). To 3.95 g (19.3 mmol) of silane **11** in a 10-mL flask, at 0–5 °C, was added 1.31 mL (9.7 mmol) of $(C_6H_5)PCl_2$. A short-path distillation head was attached to the reaction flask and the mixture was then heated at 90–95 C for 0.5 h. Subsequent flash chromatography of the crude reaction mixture on 60 g of silica gel (0.040–0.063 mm, Merck), using ether elution, gave 1.69 g (4.6 mmol) of **8** as a pale yellow oil: ^1H NMR (250 MHz, CD_2Cl_2) δ 3.78 (s, 6 H, NCH_3), 7.32–7.49 (m, 14 H), 7.64–7.74 (m, 3 H); ^{31}P NMR (C_6H_6) δ −39.6; IR (neat) 3080 (m), 3060 (m), 3035 (s) , 2970(m), 1610 (m), 1585 (m), 1478 (s), 1460 (s), 1435 (s), 1410 (s), 1364 (s), 1320 (s), 1272 (s), 1230 (s), 1150 (s), 1090 (s), 1000 (s), 805 (s), 760 (m), 720 (s), 670 (s) cm^{-1}; mass spectrum, *m/e* (relative intensity) 370 (M^+, 63), 293 (59), 238 (66), 223 (48), 147 (56), 107 (60), 77 (100), 51 (75).

Anal. Calcd for $C_{22}H_{19}N_4P$: C, 71.34; H, 5.17. Found: C, 71.42; H, 5.33.

Bis[tris(2-thienyl)phosphine]dimethylplatinum(II) (13). To a suspension of 0.17 g (0.5 mmol) of $(COD)Pt(CH_3)_2$ in 20 mL of ether, at 0 °C, was added a solution of 0.28 g (1.0 mmol) of phosphine **1** in 5 mL of ether. The resulting mixture was stirred at 0 °C for 3 h. The cold suspension was filtered. The solid obtained was dissolved in CH_2Cl_2 and then passed through a short column of silica gel. The solvent was removed from the filtrate under reduced pressure. Recrystallization of the resulting solid from CH_2Cl_2/CH_3OH afforded 0.29 g (0.36 mmol) of **13** as colorless prisms: mp 215–217 °C (dec); ^1H NMR (60 MHz, CD_2Cl_2) δ 0.57 (1:4:1 t of m, 6 H, $PtCH_3$, J_{PtH} = 71 Hz), 6.97 (m, 2 H), 7.26 (m, 2 H), 7.53 (m, 2 H); ^{31}P NMR (CH_2Cl_2) δ −3.4 (1:4:1 t, J_{PtP} = 1820 HZ); IR (KBr) 3125 (m), 2980 (m), 2960 (m), 2910 (m), 2830 (m), 1528 (s), 1420 (s), 1350 (s), 1234 (s), 1210 (s), 1105 (s), 1085 (m), 1012 (s), 865 (s), 850 (s), 760 (s), 720 (br s), 660 br s), 595 (s), 586 (s), 560 (s), 510 (br s), 455 (br s) cm^{-1}; mass spectrum, *m/e* (relative intensity) M^+ 785 absent, 770 (4), 279 (59), 113 (100); the mass spectra of the other bisphosphine complexes 14–16 only revealed peaks attributable to the coordinated phosphines.

Anal. Calcd for $C_{26}H_{24}P_2PtS_6$: C, 39.73; H, 3.08. Found: C, 39.70; H, 3.15.

Bis[tris(thiazol-2-yl)phosphine]dimethylplatinum(II) (14). A solution of 0.28 g (1.0 mmol) of phosphine **3** in 10 mL of 50% (v/v) CH_3OH/ether was added slowly to a suspension of 0.17 g (0.5 mmol) of $(COD)Pt(CH_3)_2$ in 15 mL of ether. The mixture was stirred at 0 °C for 2.5 h. Filtration of the cold reaction mixture afforded a solid which upon recrystallization from CH_2Cl_2/ether gave 0.27 g (0.34 mmol) of **14**. Complex **14** decomposed without melting at 230 °C (the sample turned amber at 185 °C): ^1H NMR (60 MHz, CD_2Cl_2) δ 0.63 (1:4:1 t of m, 6 H, $PtCH_3$, J_{PtH} = 73 Hz), 7.52 (m, 6 H), 7.83 (m, 6 H); ^{31}P NMR (CH_2Cl_2) δ 6.2 (1:4:1 t, J_{PtP} = 1820 Hz); IR (KBr) 3070 (m), 2920 (m), 2870 (m), 2795 (m), 1462 (s), 1343 (s), 1310 (s), 1190 (s), 1154 (s), 1050 (s), 1022 (s), 874 (m), 755 (s), 725 (s), 645 (s), 630 (m), 608 (m), 595 (s), 520 (s), 510 (s), 500 (s), 480 (s), 445 (s) cm^{-1}.

Anal. Calcd for $C_{20}H_{18}N_6P_2PtS_6$: C, 30.34; H, 2.29. Found: C, 30.24; H, 2.23.

Bis[tris(benzothiazol-2-yl)phosphine]dimethylplatinum(II) (15). Complex **15** was obtained in 80% yield upon treatment of $(COD)Pt(CH_3)_2$ with 2 molar equiv of phosphine **3**. Recrystallization of the complex from C_6H_6/CH_3OH afforded very fine colorless needles. Even after extensive drying in vacuo (5 days, 70 °C (0.005–0.010 torr)), ^1H NMR revealed that the crystals retained benzene. The crystalline solvate decomposed without melting above 157 °C: ^1H NMR (250 MHz, C_6D_6) δ 1.87 (1:4:1 t of m, 6 H, $PtCH_3$, J_{PtH} = 73.6 Hz), 6.81 (d of d, $ArH_{5(6)}$, *J* = 8.3, 8.3 Hz), 6.94 (d of d, 6 H, $ArH_{6(5)}$, *J* = 8.3, = 8.3 Hz), 7.18 (d, 6 H, $ArH_{4(7)}$, *J* = 8.3 Hz), 7.73 (d, 6 H, $ArH_{7(4)}$, J = 8.3 Hz); ^{31}P NMR (THF) δ 13.9 (1:4:1 t, J_{PtP} = 1792 Hz); IR (KBr) 3063 (m), 3033 (m), 2937 (m), 2889 (m), 2800 (m), 1555 (m), 1480 (m), 1455 (s), 1411 (m), 1316 (s), 1235 (m), 1193 (m), 1162 (m), 1085 (m), 1015 (m), 991 (m), 852 (s), 755 (vs), 727 (s), 676 (s), 607 (s), 585 (s), 538 (m), 521 (m), 459 (s), 442 (s), 423 (s), 410 (s), 365 (m) cm^{-1}.

Anal. Calcd for $C_{44}H_{30}N_6P_2PtS_6$: C, 48.39; H, 3.10. Found: C, 50.36; H, 3.23.

Bis[tris(1-methylimidazol-2-yl)phosphine]dimethylplatinum(II) (16). To 0.35 g (1.05 mmol) of $(COD)Pt(CH_3)_2$ in 12 mL of ether, at 0–5 °C, was added a solution of 0.58 g (2.1 mmol) of phosphine **6** in 6 mL of CH_3OH. Soon after the addition was complete the reaction mixture became homogeneous. After 15 min the mixture again became heterogeneous. The suspension was stirred at 0–5 °C for 12 h. Filtration of the cold reaction mixture afforded 0.56 g (0.7 mmol) of **16** as a white solid. Recrystallization of the solid from $CH_2Cl_2/(CH_3)_2CO$ afforded opaque crystals of **16** which retained solvent even after prolonged drying in vacuo (6 days, 78 °C (0.005–0.010 torr)). A sample of the solvated complex decomposed without melting above 212 °C: ^1H NMR (250 MHz, CD_2Cl_2) δ 0.28 (1:4:1 t of m, 6 H, $PtCH_3$, J_{PtH} = 71.9 Hz), 3.43 (br s, 18 H, NCH_3), 6.93 (br s, 6 H), 6.98 (br s, 6 H); ^{31}P NMR (Me_2SO) δ −13.9 (1:4:1 t, J_{PtP} = 1857 Hz); IR (KBr) 3127 (w), 3100 (m), 2940 (m), 2982 (m), 2809 (w), 1702 (m), 1505 (m), 1453 (s), 1408 (m), 1364 (m), 1338 (m), 1281 (s), 1275 (s), 1259 (m), 1157 (m), 1121 (m), 1078 (m), 914 (s), 860 (m), 779 (s), 749 (s), 700 (m), 681 (s), 544 (s), 514 (s), 501 (s) cm^{-1}.

Anal. Calcd for $C_{26}H_{36}N_{12}P_2Pt$: C, 40.36; H, 4.69. Found: C, 38.43; H, 4.64.

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Registry No. **1**, 24171-89-9; **2**, 80679-23-8; **3**, 80679-24-9; **4**, 80679-25-0; **5**, 80679-26-1; **6**, 80679-27-2; **7**, 80679-28-3; **8**, 80679-29-4; **9**, 32137-73-8; **10**, 35342-89-3; **11**, 35342-95-1; **12**, 80679-30-7; **13**, 80679-75-0; **14**, 80696-74-8; **15**, 80679-76-1; **16**, 80679-77-2; **18**, 80679-78-3; **19**, 80679-79-4; thiazole, 288-47-1; 2-bromothiazole, 3034-53-5; tris(2-methylphenyl)phosphine, 6163-58-2; *cis*-diethylbis[tris(thiazol-2-yl)phosphine]platinum(II), 80696-75-9; PCl_3, 7719-12-2; $(C_6H_5)PCl_2$, 644-97-3; $(C_6H_5)_2PCl$, 1079-66-9; $(COD)Pt(CH_3)_2$, 12266-92-1.