(Phosphinoalkyl)silanes. 3.[1] Poly(*o*-(diphenylphosphino)benzyl)silanes: Synthesis, Spectroscopic Properties, and Complexation at Platinum or Iridium

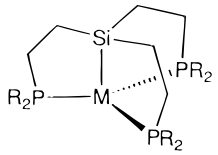
Robert A. Gossage, Geoff D. McLennan, and Stephen R. Stobart*

Department of Chemistry, University of Victoria, Victoria, British Columbia, Canada V8W 2Y2

Received October 26, 1994

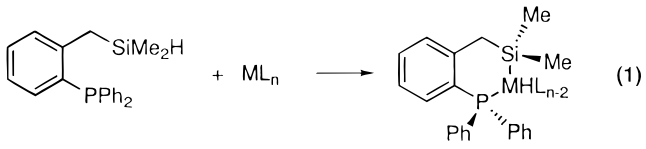
Introduction

Earlier papers[1,2] have discussed the synthesis and properties of modified silanes $PPh_2(CH_2)_nSiR_2H$ ($n = 1-3$; R = Me, Ph; *e.g.* "chelH" for $n = 2$, R = Me), in which a diorganophosphino donor site is linked through a polymethylene backbone to a silyl group that possesses an Si−H functionality. Such molecules will undergo oxidative addition at low-valent transition metal centers, affording[3−5] (phosphinoalkyl)silyl ("PSi") complexes in which Si−M bond formation is accompanied by multidentate coordination that involves one or more phosphorus donors. Thus the use of $SiH(CH_2CH_2PPh_2)_3$ (*i.e.*[1] "triPSiH") leads to encapsulation of a metal center in a cagelike assembly (*e.g.* **A**, triPSi



(A)

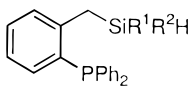
attachment at M), by which means the silyl group is *anchored* in complexes that are structurally interesting[5] and are active[6] in catalysis. To reduce the conformational flexibility of this kind of ligand framework, we have synthesized PSi precursors that use a benzyl skeleton to connect silicon to phosphorus through a three-carbon backbone that incorporates a planar benzenoid unit. The new (phosphinobenzyl)silanes so constructed have been used to isolate model "modified chelate" (mcPSi) complexes formed by "chelate-assisted"[7] oxidative addition (see eq 1) at platinum or iridium.



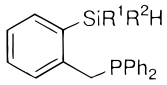
(1)

Metalation of diphenyl-*o*-tolylphosphine $P(C_6H_4Me)Ph_2$ and of benzyldiphenylphosphine $P(CH_2Ph)Ph_2$ was first explored 20 years ago by Chini *et al.*,[8] who used the *o*-(diphenylphosphino)-benzyl ($Ph_2PC_6H_4CH_2-$) carbanion to synthesize chelate-stabilized benzyl complexes of nickel, palladium, and platinum [$M(CH_2C_6H_4PPh_2)_2$, M = Ni, Pd, Pt]. At about the same time, reactivity of the isomeric (phosphinomethyl)phenyl ($Ph_2PCH_2C_6H_4-$) system was investigated[9] and found to yield (*o*-((diphenylphosphino)methyl)phenyl)trimethylsilane (*o*-$Ph_2PCH_2C_6H_4SiMe_3$) on quenching with chlorotrimethylsilane. Very recently, by the adoption of the reverse approach to P−C bond formation, treatment of chlorodiphenylphosphine with the (silylmethyl)phenyl Grignard reagents *o*-$(RCH_2)C_6H_4MgBr$ (R = $SiMe_2H$, $SiMeH_2$) was examined by Ang *et al.*[10] For either R, however, it was found that this procedure resulted in formation of an inseparable mixture of two positional isomers, *viz* the (*o*-phosphinobenzyl)silane ($Ph_2PC_6H_4CH_2R$) together with the corresponding (*o*-(phosphinomethyl)phenyl)silane ($Ph_2PCH_2C_6H_4R$). Subsequent addition of these isomeric mixtures to triosmium dodecacarbonyl afforded altogether six novel (*o*-phosphinobenzyl)silyl− and (*o*−(phosphinomethyl)phenyl)silyl−triosmium carbonyl clusters {$Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}SiR^1R^2C_6H_4CH_2PPh_2)$, $Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-}SiR^1R^2CH_2C_6H_4PPh_2)$, or $Os_3(\mu\text{-H})_3(CO)_8(\mu\text{-}SiR^1R^2C_6H_4CH_2PPh_2)$ for $R^1 = R^2 =$ Me or $R^1 =$ Me, $R^2 =$ H}, which were separated by preparative thin-layer chromatography and then high-performance liquid chromatography. Four of these products were characterized by using single-crystal X-ray diffraction, revealing that in each case phosphino−organosilane addition had occurred across a single Os−Os bond. This established that each modified silyl group so derived is able to function as a *bridging* PSi ligand (though **not** *chelate* (*cf.* eq 1), as was claimed[10]).

We report below that, by using appropriate[8] organolithium reagents, it is possible to prepare both pure (*o*-(diphenylphosphino)benzyl)dimethylsilane (**1**) and pure (*o*-((diphenylphosphino)methyl)phenyl)dimethylsilane (**2**), *i.e.* independently,



1 $R^1 = R^2 =$ Me



2 $R^1 = R^2 =$ Me

3 $R^1 =$ Me, $R^2 = CH_2C_6H_4PPh_2$

4 $R^1 = R^2 = CH_2C_6H_4PPh_2$

uncontaminated by one another; that the same methodology may be extended to the synthesis of poly(*o*-phosphinobenzyl)silanes; and that ligand precursors belonging to this (phosphinobenzyl)-silane family will indeed add at a single metal center in a chelating mode, to afford analogues of the prototypal[6] PSi complexes. The trifunctional ligand precursor $SiH(Me)[CH_2(o\text{-}(PPh_2)C_6H_4)]_2$ (*i.e.* "mcbiPSiH") is also shown to be accessible *via* dilithiation followed by phosphination of the new bis(bromobenzyl)silane $SiH(Me)[CH_2(o\text{-}BrC_6H_4)]_2$. Restricted conformational mobility of the backbone connecting Si to P in these mcPSi systems may be expected to engender steric constraints on substrate approach in the vicinity of a reactive metal site that will modify catalyst selectivity.[6]

Experimental Section

All manipulations were conducted under dry dinitrogen gas using standard inert-atmosphere techniques. Manipulation of solid lithium salts was carried out in an argon-filled glovebox. Solvents were dried and redistilled immediately prior to use. Chlorosilanes, aryl bromides,

(1) Part 2: Joslin, F. L.; Stobart, S. R. *Inorg. Chem.* **1993**, *32*, 2221.
(2) Holmes-Smith, R. D.; Osei, R. D.; Stobart, S. R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 861.
(3) Auburn, M. J.; Stobart, S. R. *Inorg. Chem.* **1985**, *24*, 318.
(4) Auburn, M. J.; Holmes-Smith, R. D.; Stobart, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1314.
(5) Joslin, F. L.; Stobart, S. R. *J. Chem. Soc., Chem. Commun.* **1989**, 504.
(6) Stobart, S. R.; Grundy, S. L.; Joslin, F. L. U.S. Patent 4 950 798, 1990; Canadian Patent 1 327 365, 1994.
(7) Holmes-Smith, R. D.; Stobart, S. R.; Cameron, T. S.; Jochem, K. *J. Chem. Soc., Chem. Commun.* **1981**, 937. Grundy, S. L.; Holmes-Smith, R. D.; Stobart, S. R.; Williams, M. A. *Inorg. Chem.* **1991**, *30*, 3333.
(8) Fantucci, P.; Chini, P.; Canziani, F. *Gazz. Chim. Ital.* **1974**, *104*, 249.
(9) von Abicht, H.-P.; Issleib, K. *Z. Anorg. Allg. Chem.* **1976**, *422*, 237.
(10) Ang, H. G.; Chang, B.; Kwik, W. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2161.

0020-1669/96/1335-1729$12.00/0

chlorodiphenylphosphine, and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) were commercial products (Aldrich Co.). NMR spectra were recorded using a Bruker WM250 Fourier transform spectrometer.

Synthesis of Compounds. A. Ligand Precursors. 1. (*o*-(Diphenylphosphino)benzyl)dimethylsilane, 1. To a slurry of *o*-tolyldiphenylphosphine (2.34 g, 8.47 mmol) in hexanes (30 mL) was added from a dropping funnel a mixture of tmeda (1.5 mL) and $LiBu^n$ (5.6 mL, 9.0 mmol) in hexanes (20 mL). Appearance of an orange color was followed by precipitation of a bright yellow solid; after stirring (2 h), solvent was removed and the residue was washed with hexanes. This material (1.00 g, 2.84 mmol) was suspended in hexanes (25 mL), and after the mixture was cooled to 0 °C, chlorodimethylsilane (1.3 mL, 11.7 mmol) was run in, discharging the color and precipitating a white solid. After stirring (14 h), volatile material was pumped away, leaving a cloudy, pale yellow oil. This was dissolved in hexanes, the mixture was filtered, and the filtrate was then reduced in volume and finally distilled under reduced pressure (200 °C/0.5 mmHg) to afford the product as a colorless, viscous oil (52%), shown by IR and NMR spectroscopy to be one component of the mixture (*i.e.* of compounds **1** and **2**) reported elsewhere.[10]

2. (*o*-((Diphenylphosphino)methyl)phenyl)dimethylsilane, 2. To a solution in Et_2O (20 mL) of[9] (*o*-bromobenzyl)diphenylphosphine (0.63 g, 1.78 mmol) was added drop by drop *n*-butyllithium (3 mL, 1.6 M in hexanes) at 20 °C. During this operation, the initially colorless solution became cloudy and turned yellow, ultimately affording a deep chrome-yellow pigmented suspension in an orange-red solution. The reaction mixture was subsequently stirred for 3 h, and then the ether was removed under reduced pressure to leave an orange powder; this was washed with dry hexanes (35 mL) and then suspended in dry benzene (30 mL), whereupon chlorodimethylsilane (3.0 mL, 35 mmol) was run in over 5 min, during which the color was discharged and a white precipitate was deposited. The resulting mixture was heated to 45 °C and then stirred (4 h); after filtration through a glass frit and removal of volatiles, the product remained as a clear, colorless oil (0.25 g, 58%), shown by IR and NMR spectroscopy to be the second (*vs* **1**, see preparation A1 above) component of the isomeric mixture reported elsewhere.[10]

3. Bis(*o*-(diphenylphosphino)benzyl)methylsilane, mcbiPSiH, 3. Method I. *n*-Butyllithium (2.5 mL, 1.6 M in hexanes) was added dropwise to a solution of *o*-tolyldiphenylphosphine (1.0 g, 3.6 mmol) in dry hexanes (40 mL) and tmeda (0.6 mL). The mixture turned deep orange and deposited an orange solid within 5 min. After stirring (4 h, 20 °C), volatile material was removed, leaving an orange solid; redissolution of the latter in benzene (30 mL) was followed by rapid addition of a stoichiometric deficit of dichloromethylsilane (0.1 mL, 0.74 mmol), whereupon the mixture became warm and faded in color to light orange. After overnight stirring, removal of volatiles left an orange oil; this was redissolved in 2:1 benzene/hexanes (30 mL), leaving a white precipitate and affording a yellow solution, which was filtered and then reduced in volume to a brown-yellow oil. A ^{31}P NMR spectrum of the latter revealed the presence of regenerated *o*-$MeC_6H_4PPh_2$, which was removed by sublimation (150 °C/10^{-2} mmHg). This left a dark brown oil, which was dissolved in benzene (20 mL); the solution was then filtered through a plug of 1:1 Celite/silica gel. Removal of volatiles yielded the product as a pale yellow oil (0.41 g, 38%) that set to a glassy semisolid below 20 °C.

Method II. To a solution in Et_2O (20 mL) of (2-bromobenzyl)-magnesium chloride (23.4 mmol) (prepared by Grignard synthesis from commercial 2-bromobenzyl bromide) was added drop by drop dichloromethylsilane (1.0 mL, 9.6 mmol) also in Et_2O (15 mL), and the mixture was then refluxed (12 h). Filtration and then removal of solvent under vacuum left orange material, which was extracted with hexanes (50 mL). Evaporation of the solvent left a yellow, oily liquid, which was distilled under reduced pressure (180 °C/10^{-2} mmHg) to yield colorless, oily bis(2-bromobenzyl)methylsilane (72%), which was characterized by IR, NMR, and mass spectroscopy: ν_{Si-H} 2125 vs cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.55−6.91 (C_6H_4), 4.07 (Si*H*), 2.41 (CH_2, ^3J 2.9 Hz), 0.09 (CH_3, ^3J 2.6 Hz); ^{29}Si NMR δ −11.22 *vs* $SiMe_4$; MS M^+ 381 (M_{calc} 381). This precursor (11.7 mmol) was dissolved in Et_2O (40 mL), the solution was cooled to −78 °C, and $LiBu^n$ (15.6 mL, 25 mmol) was slowly added by syringe. Warming to room temperature followed by gentle reflux (3 h) and then stirring (3 h) afforded a clear yellow solution, to which was added PPh_2Cl (4.5 mL, 25 mmol), resulting in an exothermic reaction. After reflux (12 h), stirring (12 h), filtration, and removal of solvent, a pale yellow viscous liquid remained which was shown by ^{31}P NMR spectroscopy to be the product (**3**) contaminated with unchanged PPh_2Cl, together with a minor proportion (*ca.* 20% *vs* **3**) of a third constituent (identified by its chemical shift as PBu^nPh_2), traces of which persisted after repeated distillation at reduced pressure.

4. Tris(*o*-(diphenylphosphino)benzyl)silane, mctriPSiH, 4. Using procedures that paralleled those detailed in preparation A3, (method I) above, lithiation of *o*-$MeC_6H_4PPh_2$ (3.00 g, 10.9 mmol) followed by addition of trichlorosilane (0.2 mL, 2.0 mmol) afforded a product which after purification was recovered as a pale yellow wax (1.02 g, 56%). Anal. Found: C, 79.7; H, 5.7. Calcd for $C_{57}H_{49}P_3Si$: C, 80.1; H, 5.7.

B. Platinum and Iridium Complexes. 1. Bis[(*o*-(diphenylphosphino)benzyl)dimethylsilyl]platinum(II), Pt(mcchel)$_2$, 5. Drop by drop addition of a solution of silane **1** (150 mg, 0.44 mmol) in benzene (4 mL) to $Pt(cod)Cl_2$ (81 mg, 0.22 mmol) dissolved in a mixture of benzene (7 mL) and NEt_3 (4 mL) was accompanied by a change from colorless to yellow and deposition of a fluffy precipitate. After agitation for 90 min, removal of volatiles under reduced pressure left a yellow oil, which was redissolved in hexanes (5 mL). Elution with hexanes through a Florisil column (1 × 3 cm) was followed by evaporation of solvent to give an off-white crude product, which was recrystallized from 1:1 pentane/CH_2Cl_2 as colorless crystals (25 mg, 13%). Anal. Found: C, 58.8; H, 5.2. Calcd for $C_{42}H_{44}P_2PtSi_2$: C, 58.5; H, 5.4.

2. [Bis(*o*-(diphenylphosphino)benzyl)methylsilyl]platinum(II) Chloride, Pt(mcbiPSi)Cl, 6. In a manner paralleling that described in preparation B1 above, admixture of $Pt(cod)Cl_2$ (35 mg, 0.09 mmol), NEt_3 (0.7 mL), and silane **3**, *i.e.* mcbiPSiH (56 mg, 0.1 mmol), in benzene (8 mL) yielded a light yellow, oily material, which was extracted with CH_2Cl_2 (10 mL); filtration through a glass sinter led to isolation of a sticky yellow solid, which was recrystallized (1:1 hexanes/CH_2Cl_2) to afford the pure product as a white powder (20 mg, 27%). Anal. Found: C, 54.6; H, 4.3. Calcd for $C_{39}H_{35}ClP_2PtSi\cdot0.5CH_2Cl_2$: C, 54.7; H, 4.2.

3. Chlorohydrido[tris(*o*-(diphenylphosphino)benzyl)silyl]iridium-(III), Ir(mctriPSi)H(Cl), 7. Silane **4**, *i.e.* mctriPSiH (88 mg, 0.10 mmol), was added directly to a solution of $[Ir(cod)Cl]_2$ (35 mg, 0.05 mmol) in THF (7 mL). The mixture was stirred for 2 h, during which the color faded from orange to light yellow. After evacuation to remove volatiles, a light yellow product remained, which was recrystallized from chloroform/hexanes as a white powder (101 mg, 91%). Anal. Found: C, 60.0; H, 4.5. Calcd for $C_{57}H_{49}ClIrP_3Si\cdot0.5CHCl_3$: C, 60.4; H, 4.6.

Results

Synthesis of (phosphinoaryl)silanes using the reaction of the Grignard reagent *o*-$BrMgC_6H_4CH_2SiMe_2H$ with PPh_2Cl is reported[10] to lead *via* exchange metalation to formation of an inseparable mixture of compounds **1** and **2**, which are positional isomers. By contrast, we find that lithiation of *o*-tolyldiphenylphosphine in the presence of tmeda or of (*o*-bromobenzyl)-diphenylphosphine, followed by quenching with chlorodimethylsilane, provides each of these two compounds independently (Scheme 1), *i.e.* uncontaminated by one another. In either reaction, the required organolithium reagent, which is not very soluble, is formed as a deep orange-yellow suspension: in each case, discharge of this characteristic color is a good indicator of the progress of the reaction. Each product (**1** or **2**) was recovered as a colorless, rather viscous oil in *ca.* 50% yield; survival of the silyl (*i.e.* Si−H) functionality was obvious from strong IR absorption near 2120 cm^{-1} and by observation of ^1H NMR signals at δ 4.14 (**1**) and 4.60 (**2**), δ(Si*H*), as multiplets that integrated correctly *vs* alkyl protons. Further characterization was provided by ^{13}C NMR (alkyl carbons) as well as by ^{29}Si and ^{31}P NMR chemical shifts (Table 1). The assignments proposed earlier by Ang *et al.*[10] on the basis of NMR data (quoted to 5 significant figures) for the isomer mixture **1**/**2** are consistent with the spectra observed for **1** and **2**, apart from the

Scheme 1

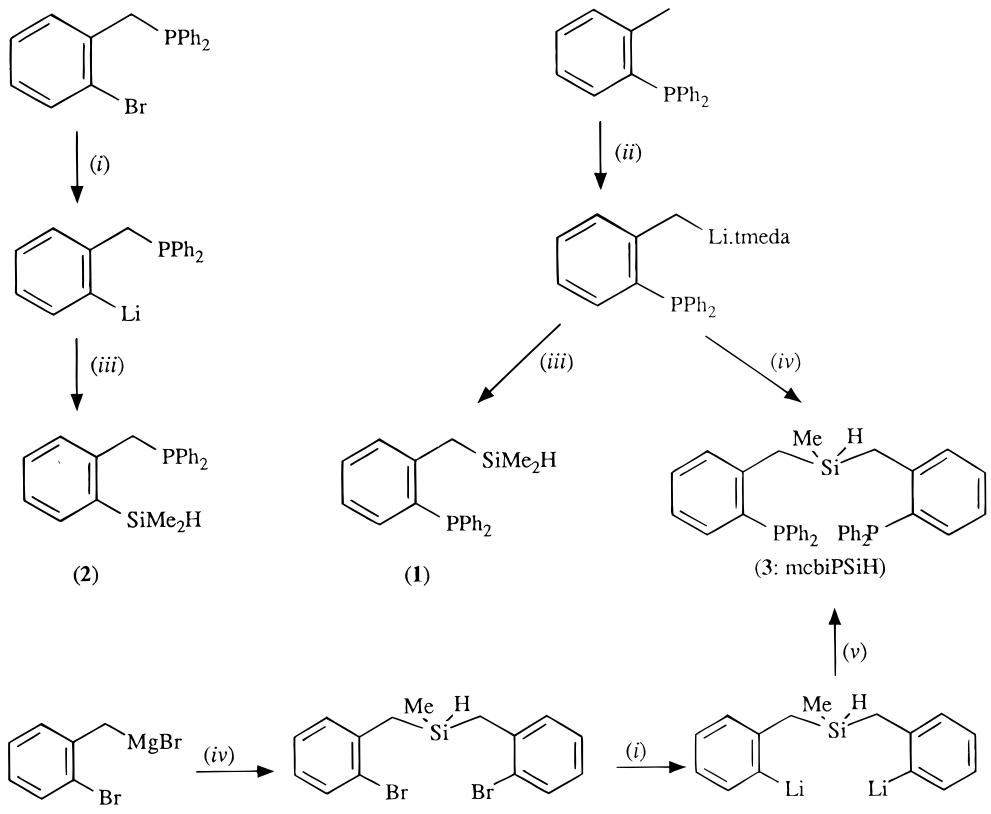


Table 1. NMR Data for (Phosphinobenzyl)silanes and (Phosphinobenzyl)silyl Complexes[a]

			^{1}H NMR[c]					^{13}C NMR[c]		
cmpd	$\delta(^{31}P)$[b]	$\delta(^{29}Si)$[c]	$\delta(CH_2Si)$	$^3J(CH_2SiH)$[d]	$\delta(CH_3Si)$	$^3J(CH_3SiH)$[d]	δ(SiH)	$\delta(CH_2Si)$	$\delta(SiCH_3)$	$^1J(CH_2P)$[d]
1	−14.1	−11.2	2.51	3.3	0.24	3.6	4.14	23.0	−4.0	
3	−14.0	−7.2	2.64	3.0[e]	0.02	3.6	4.01	22.00	−5.7	21.9
4	−14.1	−3.7	2.48	3.4	n.a.[f]	n.a.	4.21	20.8	n.a.	24.6
5	+20.9[g]	+23.1[h]	1.88[i]	n.a.	0.25[j]	n.a.	n.a.	31.9	5.2	n.r.
6	+22.3[k]	n.m.	2.30[l]	n.a.	−0.53[m]	n.a.	n.a.	n.m.	n.m.	n.m.
7[n]	−5.3,[o] −11.4[p]	n.m.	2.38	n.a.	n.a.	n.a.	n.a.	n.m.	n.m.	n.m.

[a] All spectra recorded in $CDCl_3$ solution: resonances due to phenyl substituents were observed in the range δ 8.0−6.4 (^{1}H) or δ 135−125 (^{13}C), showing multiplet structure which was not analyzed in detail. [b] Relative to external 85% H_3PO_4. [c] Relative to external $SiMe_4$. [d] Coupling constants in Hz. [e] $^4J(CH_2SiCH_3)$ = 10.3 Hz. [f] n.a. = not applicable, n.r. = not resolved, n.m. = not measured. [g] $^1J_{PtP}$ = 1458 Hz. [h] $^2J_{SiP(trans)}$ = 142 Hz; $^2J_{SiP(cis)}$ = 22 Hz. [i] $^3J_{PtH}$ = 31.0 Hz; $^4J_{PH}$ = 3.7 Hz. [j] $^3J_{PtH}$ = 13.2 Hz. [k] $^1J_{PtP}$ = 2908 Hz. [l] $^3J_{PtH}$ = 54.6 Hz. [m] $^3J_{PtH}$ = 25.6 Hz. [n] δ_{Ir-H} = −9.55; $^2J_{PH(trans)}$ = 126 Hz; $^2J_{PH(cis)}$ = 20.2 Hz. [o] P trans to P; non-first-order spectra; see text. [p] P trans to H.

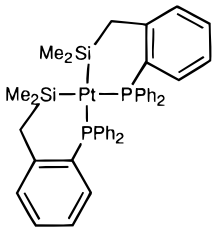
^{29}Si chemical shift for compound **2**, which is at −22.1 ppm (not −10.6 as suggested[10]). The downfield shift in $\delta(^{29}Si)$ of 10 ppm (**2** *vs* **1**) reflects the structural change from a trialkylsilane to a dialkylarylsilane.

Our interest in precursors to cagelike coordination environments led us to examine the possibility of polysubstitution at Si, using the (diphenylphosphino)benzylcarbanion formed by lithiation of *o*-tolyldiphenylphosphine to effect alkylsilyl synthesis. With both dichloromethylsilane and trichlorosilane, analogues of biPSiH and triPSiH were obtained in moderate yield. An alternate route to mcbiPSiH (**3**) is provided by the action of (2-bromobenzyl)magnesium chloride on dichloromethylsilane; this affords in good yield bis(2-bromobenzyl)methylsilane as a colorless oil, which after dilithiation at low temperature followed by reaction with chlorodiphenylphosphine gave the product. The two compounds (**3** and **4**, "mcbiPSiH" and "mctriPSiH", respectively) are waxy semisolids, which were initially characterized by IR and NMR spectroscopy (^{1}H, ^{13}C, ^{29}Si, ^{31}P): the data are collected in Table 1, and the chemistry is summarized in Scheme 1.

Compounds **1**−**4** were further characterized by using mass spectrometry, which provided in particular an obvious distinction between the positional isomers **1** and **2**, which have previously only been handled[10] as an inseparable mixture. Exact mass determination *via* peak matching further confirmed the identification of **3** (found 594.2046; calcd 594.206 16) and **4** (found 854.2815; calcd 854.2816). Parent ions were weak but observable in all four spectra. Consistent with similar magnitudes of Si−C *vs* P−C bond strengths, no dominant process is apparent in subsequent fragmentation: base peaks at *m/z* 135 (**1**), 149 (**2**), 319 (**3**), and 275 (**4**) correspond to nominal loss of PPh_2-$CH_2^\bullet$, $PPh_2^\bullet$, $PPh_2C_6H_4CH_2^\bullet$, and $Si(CH_2C_6H_4PPh_2)_2H^\bullet$, respectively. Thus for **2** the most abundant fragment is nominally an *o*-silylbenzyl cation (although PPh_2^+ is also prominent, *m/z* 185,

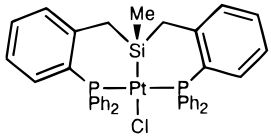
arising from $Me_2SiHC_6H_4CH_2^{\bullet}$ elimination). For mcbiPSiH (**3**), loss of one phosphinoaryl "arm" gives rise to by far the most important ion in the spectrum, while for mctriPSiH (**4**), the base peak corresponds to an *o*-phosphinobenzyl ion although there are several other major fragments, notably at *m/z* 197, 183, and 165. The latter are also present in the spectrum of **1**, where they may arise through loss of PhH (to *m/z* 256) and then $SiMe_2H^{\bullet}$ or $SiMe_2HCH_2^{\bullet}$ and where the base peak may arise from $PPh_2^{\bullet}$ cleavage to give a reactive phenylcarbonium ion that undergoes benzylic rearrangement involving CH_2 loss to $C_6H_4CH_2SiMeH^+$ (*m/z* 135). This provides the most obvious analytical difference between the spectrum of **1** and that of **2**: *m/z* 149 which is missing completely for **1** is *ca.* 4 times as intense as *m/z* 135 for **2**. Interestingly $PPh_2C_6H_4CH_2^+$, which is the base peak for **4**, is reduced for **3** and can only be detected by using chemical ionization for **1**.

Under conditions identical with those that lead[7] to formation of $Pt(chel)_2$ from chelH (*i.e.* $PPh_2CH_2CH_2SiMe_2H$), reaction of compound **1** with $Pt(cod)Cl_2$ led to isolation of the colorless, crystalline analogue *cis*-$Pt(SiMe_2CH_2C_6H_4PPh_2)_2$, **5** (*cf.* eq 1),



(5)

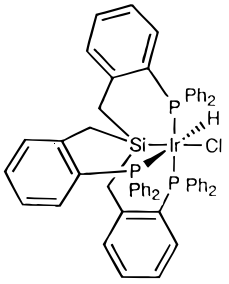
for which the low value of $^1J_{PtP} = 1459$ Hz is fully consistent[7] with P trans to Si. The cis stereochemistry was also obvious from the ^{29}Si spectrum, in which both trans (142 Hz) and cis (22 Hz) coupling to P were resolved. Coupling of silylmethyl hydrogens (^3J) to ^{195}Pt was also[7] evident (13 Hz). A similar reaction using mcbiPSiH (**3**) afforded a further white product (as a dichloromethane hemisolvate, NMR) identified by microanalysis and NMR spectroscopy as another d^8 Pt(II) complex Pt(mcbiPSi)Cl, **6**. The value for $^1J_{PtP}$ of 2908 Hz is typical for



(6)

phosphorus nuclei trans to one another. The benzyl CH_2 proton resonances are also structurally informative for compounds **5** and **6**: in the former (δ 1.88, Table 1) coupling to Pt and to trans P are obvious, while for the mcbiPSi complex $^3J_{PtH}$ is nearly twice as large (*i.e.* disposed trans to the weak ligand Cl *vs* P in **5**) whereas cis coupling to P is small and is not detected.

Quadridentate coordination of the mctriPSi unit was anticipated[5,6] and so was investigated around octahedral Ir(III). Addition of compound **4** to a solution of the well-known labile dimeric precursor $[Ir(cod)Cl]_2$ led to isolation in virtually quantitative yield of the pale yellow complex IrH(mctriPSi)Cl (**7**: chloroform hemisolvate, NMR). The ^{31}P NMR spectrum



(7)

of this compound showed an A_2B pattern (Table 1) that was not exactly first-order but was recognizable as a distorted doublet/triplet with a small (*i.e.* cis) $^2J_{PP}$. Accordingly, the δ(Ir*H*) (which at −9.5 ppm is in the range for H trans to P rather than Cl) is split into a doublet of triplets by coupling to both trans (^2J 126 Hz) and cis (20 Hz) P atoms, so that the stereochemistry is unambiguous with mctriPSi occupying four all-cis sites and H, Cl trans to P, Si, respectively.

Discussion

The lithiation reactions described provide efficient steps for synthesis of a new family of PSi ligand precursors[6] in which the connectivity between Si and P is made through a benzyl framework. Polysubstitution at Si affords mcbiPSiH and mctriPSiH (*i.e.* **3** and **4**), which can lead *via* hydrosilylation[1−6] to polydentate complexation. The ability of silanes **1**, **3**, and **4** to undergo such chemistry (eq 1) has been demonstrated by synthesis of model complexes of Pt(II) and Ir(III). PSi coordination established in this way is clearly *chelate*, rather than[10] *bridging*; the NMR properties of compounds **5**−**7** render the stereochemistry in each case unequivocal, with the arrangements adopted by **5** and **7** resembling those reported earlier for prototypal PSi analogues.[5,7] We expect that the polydentate silyl attachment at a transition metal center of mcbiPSi or mctriPSi will present a more rigid ligand profile than is imparted by the prototypal polymethylene systems[5,6] biPSi and triPSi: constraining the carbon atoms β and γ (to Si) to planarity (sp^2 character) should drastically reduce the mobility of the connecting backbone. The effect of such rigidity on substrate approach, reactivity, and catalysis[6] is under investigation.

Acknowledgment. We thank the NSERC of Canada for funding.

IC941230F