collected at room temperature. The intensities of three intensity standards showed only minor fluctuations over the period of data collection. Data were corrected for Lorentz and polarization effects and empirically for absorption (ψ-scan method), and a total of 3142 data were used in the structure refinement.

Structure Solution and Refinement. The three osmium atoms were located by direct methods (SHELXTL PLUS[23]). Alternating cycles of least-squares full-matrix refinement followed by difference Fourier synthesis located all the other non-hydrogen atoms with a convergence to $R = 0.0514$ and $R_w = 0.0512$ (see Table III for weighting scheme). All non-hydrogen atoms were refined anisotropically and, although the hydrogen atoms were not located, those of the two ethyl groups were included in idealized positions (C-H = 0.95 Å) and with a common isotropic temperature factor, $U = 0.08$ Å^2, in the final stages of refinement. The hydrogen positions were finally fixed for the last cycle of refinement. Atomic scattering factors used were those contained in the SHELXTL PLUS package.[23]

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Note Added in Proof. Since this paper was submitted, compound **3a** has been reported to be formed by photolytic decarbonylation of $[Os_3H(\mu\text{-}CHCHNEt_2)(CO)_{10}]$ (Figure 4).[24]

Registry No. **1**, 55073-02-4; **2**, 105286-42-8; **3a**, 105286-40-6; **3b**, 105286-41-7; **4**, 105286-38-2; **5**, 105286-39-3; **7a**, 118299-47-1; **7b**, 118299-48-2; $[Os_3(CO)_{10}(MeCN)_2]$, 61817-93-4; $[Os_3(C_2H_2)(CO)_{10}]$, 57373-35-0; $[Os_3H(PMe_2PhC_2H)(CO)_9]$, 82740-30-5; HC≡CH, 74-86-2.

Supplementary Material Available: More detailed crystallographic experimental and tables of all bond lengths and angles, anisotropic displacement parameters for non-hydrogen atoms, and hydrogen atom coordinates (7 pages); a listing of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Coordinated Ligand Basicity. Synthesis and Reactivity of Terminal Phosphide Complexes of Iridium That Also Contain an Amide Donor

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The reaction of stoichiometric amounts of $LiPR_2$ (R = Ph and *m*-tol) with the square-pyramidal complex $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (1) generates the new terminal phosphide complexes $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$ (**2a**, R = Ph; **2b**, R = *m*-tol). On the basis of solution spectroscopic data, the structure is proposed to be intermediate between trigonal bipyramidal and square pyramidal. Although the geometry at the phosphide phosphorus is ambiguous (pyramidal versus planar), the $^{31}P\{^1H\}$ NMR chemical shift can be interpreted as a result of a dynamic equilibrium between the two forms assisted by the lone pair on the amide nitrogen of the ancillary tridentate ligand. The phosphide is nucleophilic and undergoes intermolecular methylation with methyl iodide; the stereochemistry of the octahedral methylated material is shown to be *trans*-CH_3-I-*mer*-$Ir(CH_3)I(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$.

During the last 2 decades, interest in tertiary phosphine complexes (L_nM-PR_3) of the transition metals has grown tremendously, due in part to the observation that many of these derivatives are catalyst precursors for such industrially important processes as hydrogenation, hydroformylation, and polymerization.[1] As a result, the number of phosphine-containing complexes is now legion.[2]

In addition to the well-studied phosphines, ligands having other valences of phosphorus are known but less studied. These include metalated phosphoranes (L_nM—PR_4),[3] phosphides (L_nM—PR_2),[4-20] and phosphinidenes (L_nM=PR).[21-25] Although mononuclear phosphorane and phosphinidene complexes are still extremely rare, the

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chemistry of transition-metal phosphides has become a rapidly growing research area. A wide range of metals are known to bind terminal phosphide ligands, but very few examples of the group 9 metal iridium have been reported in the literature.[10-13] In this paper, we detail the synthesis and characterization of the five-coordinate organoiridium(III) diarylphosphide complexes of the formula $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$ (R = phenyl, *m*-tolyl).[6] Since these complexes also contain the potentially basic amide donor,[7] it was of interest to compare its relative nucleophilicity to that of the phosphide donor.

Experimental Section

General Information. All manipulations were performed under prepurified nitrogen in a Vacuum Atmospheres HE-553-2 glovebox equipped with a MO-40-2H purification system or in standard Schlenk-type glassware. Iridium trichloride hydrate was obtained on loan from Johnson Matthey and used directly in the synthesis of $[Ir(COE)_2Cl]_2$ (COE = cyclooctene).[26] The complexes $Ir(R)I[N(SiMe_2CH_2PPh_2)_2]$ (R = CH_3, Ph, CH_2Ph) were prepared by published procedures.[27,28] $LiPPh_2$ and $LiP(m\text{-tol})_2$[29] were prepared by dropwise addition of *n*-butyllithium in hexane (1.6 M, Aldrich) to a hexane solution of $HPPh_2$ and $HP(m\text{-tol})_2$, respectively. After several washings with hexanes, the resultant lemon-yellow powders were used directly in the synthesis of $Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$ and $Ir(CH_3)P(m\text{-tol})_2[N(SiMe_2CH_2PPh_2)_2]$.

Toluene and hexanes were dried and deoxygenated by distillation from sodium benzophenone ketyl under argon. Tetrahydrofuran (THF) was predried by refluxing over CaH_2 and then distilled from sodium benzophenone ketyl under argon. $^{13}CH_3I$ (99.7 atom % ^{13}C) and CD_3I (98 atom % D) were obtained from MSD and used as received. Deuterated benzene (C_6D_6, 99.6 atom % D), purchased from MSD, was dried over activated 4-Å molecular sieves, vacuum transferred, and degassed by freeze–pump–thawing several times before being used.

Melting points were determined on a Mel-Temp apparatus in sealed capillaries under nitrogen and are uncorrected. Carbon, hydrogen, and nitrogen analyses were performed by Mr. P. Borda of this department.

^1H NMR spectra were recorded on a Bruker WH-400 spectrometer in C_6D_6 and were referenced to C_6D_5H at 7.15 ppm; nuclear Overhauser effect (nOe) experiments were run on the WH-400 by using standard pulse sequences on the Aspect 2000 computer. $^{31}P\{^1H\}$ NMR spectra were run at 121.4 MHz on a Varian XL-300 spectrometer, and all ^{31}P chemical shifts were referenced to external $P(OMe)_3$ set at 141.00 ppm relative to 85% H_3PO_4.

$Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$: General Procedure. A solution of $LiPR_2$ (R = phenyl, *m*-tolyl) in THF (5 mL) was added dropwise while stirring to $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ in toluene (10 mL). The initially deep green solution immediately turned dark purple. After being stirred for an hour, the solution was filtered through Celite in order to remove LiI. The solvent was removed in vacuo, and the resulting powder was crystallized from toluene and hexane at −30 °C which yielded dark purple crystals of $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$.

$Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$ (2a): $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (0.24 g, 0.28 mmol); $LiPPh_2$ (0.05 g, 0.31 mmol). ^1H NMR (C_6D_6, 400 MHz, δ): $Si(CH_3)_2$, −0.13 (s), 0.68 (s); $IrCH_3$, 0.72 (q, ^3J_P = 4.0 Hz); $SiCH_2P$, 1.82 (dt, J_{app} = 4.6 Hz, $^2J_{gem}$ = 12.0 Hz), 2.36 (dt, J_{app} = 4.8 Hz); $P(C_6H_5)_2$, 7.10 (m, para/meta), 7.85 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz, δ): CH_2PPh_2, 10.30 (d, ^2J_P = 34.8 Hz); $IrPPh_2$, 105.65 (t). Anal. Calcd for $IrC_{43}H_{49}P_3NSi_2$: C, 56.07; H, 5.36; N, 1.52. Found: C, 55.80; H, 5.35; N, 1.40.

$Ir(CH_3)P(m\text{-tol})_2[N(SiMe_2CH_2PPh_2)_2]$ (2b): $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (0.22 g, 0.25 mmol); $LiP(m\text{-tol})_2$ (0.05 g, 0.26 mmol). ^1H NMR (C_6D_6, 400 MHz, δ): $Si(CH_3)_2$, −0.13 (s), 0.70 (s); $IrCH_3$, 0.75 (q, ^3J_P = 4.0 Hz); $SiCH_2P$, 1.75 (dt, J_{app} = 4.6 Hz, $^2J_{gem}$ = 13.3 Hz), 2.36 (dt, J_{app} = 4.7 Hz); $P(C_6H_5CH_3)_2$ 2.10 (s); $P(C_6H_5)_2$, 7.11 (m, para/meta), 7.90 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, 109.31 MHz, external reference, $P(OMe)_3$, was set at +141.0 ppm, δ): CH_2PPh_2, 15.48 (d, ^2J_P = 34.7 Hz); $IrP(m\text{-tol})_2$, 117.84 (t). Anal. Calcd for $IrC_{45}H_{53}P_3NSi_2$: C, 56.94; H, 5.63; N, 1.48. Found: C, 56.70; H, 5.62; N, 1.42.

$Ir(CH_3)I(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$ (3). Method 1. This preparation involved the vacuum transfer of an excess (at least fivefold) of degassed CH_3I at −10 °C to a toluene solution (10 mL) of $Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$ (0.25 g, 0.27 mmol). The solution was allowed to warm to room temperature, during which time the original purple color changed to light yellow. After the solution was stirred for 0.5 h, the solvent was removed in vacuo. Recrystallization of the resultant powder from toluene yielded yellow crystals. Yield: 0.21 g (75%). Anal. Calcd for $IrC_{44}H_{52}NP_3Si_2I\cdot{}^1/_4C_7H_8$: C, 50.59; H, 5.01; N, 1.29. Found: C, 50.40; H, 5.08; N, 1.20. (The amount of C_7H_8 in the sample was determined from its ^1H NMR spectrum.) ^1H NMR (C_6D_6, 400 MHz, δ): $Si(CH_3)_2$, 0.52 (s), 0.75 (s); $IrCH_3$, 0.80 (q, ^3J_P = 5.3 Hz); $SiCH_2P$, 2.24 (dt, J_{app} = 6.6 Hz, $^2J_{gem}$ = 14.7 Hz), 2.50 (dt, J_{app} = 6.3, Hz); PCH_3Ph_2, 1.58 (d, ^2J_P = 10.6 Hz); $P(C_6H_5)_2$, 7.07 (m, para/meta), 7.38, 8.50 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz, δ): CH_2PPh_2, −17.67 (d, ^2J_P = 18.6 Hz); PCH_3Ph_2, −36.60 (t).

Method 2. To a solution of $Ir(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$ (0.05 g, 0.05 mmol) in toluene (5 mL) was vacuum transferred excess (at least fivefold) degassed CH_3I at −10 °C. The solution was stirred for 0.5 h and the solvent removed in vacuo to give a yellow oil. The addition of toluene/hexane resulted in yellow crystals. Yield: 0.04 g (65%).

$Ir(CH_3)I(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$ (4). A toluene solution (1 mL) of PPh_2Me (0.01 g, 0.05 mmol) was added dropwise to a solution (5 mL) of $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (0.04 g, 0.05 mmol) at room temperature. The original deep green colour changed to light yellow. The solvent was removed in vacuo. Recrystallization of the resultant powder from toluene yielded yellow crystals. Yield: 0.04 g (70%). Anal. Calcd for $IrC_{44}H_{52}NP_3Si_2I\cdot{}^1/_4C_7H_8$: C, 50.59; H, 5.01; N, 1.29. Found: C, 50.68; H, 5.42; N, 1.17. ^1H NMR (C_6D_6, 400 MHz, δ): $Si(CH_3)_2$, 0.46 (s), 0.75 (s); $IrCH_3$, 1.43 (dt, $^3J_{PCH_3Ph_2}$ = 20.0 Hz, $^3J_{CH_2PPh_2}$ = 6.0 Hz); $SiCH_2P$, 1.58 (dt, J_{app} = 6.6 Hz, $^2J_{gem}$ = 13.3 Hz), 2.03 (dt, J_{app} = 6.3 Hz); PCH_3Ph_2, 1.92 (d, ^2J_P = 6.7 Hz); $P(C_6H_5)_2$, 7.33 (m, para/meta), 7.80, 8.06 (m, ortho).

$Ir(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$. A solution of PCH_3Ph_2 (0.01 g, 0.05 mmol) in toluene (2 mL) was added dropwise to a toluene solution (5 mL) of $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PPh_2)_2]$ (0.05 g, 0.06 mmol). After the solution was stirred for an hour, the solvent was removed in vacuo. Yellow crystals were obtained upon crystallization from hexanes. ^1H NMR (C_6D_6, 400 MHz, δ): $Si(CH_3)_2$, 0.18 (s); $SiCH_2P$, 1.87 (t, J_{app} = 5.3 Hz); PCH_3Ph_2, 1.37 (d, $^2J_{P,H}$ = 6.7 Hz); $P(C_6H_5)_2$, 6.88 (m, para/meta), 7.65 (m, ortho). $^{31}P\{^1H\}$ NMR (C_6D_6, 121.421 MHz, δ): CH_2PPh_2, 25.30 (d, ^2J_P = 22.8 Hz); PCH_3Ph_2, −1.79 (t). Anal. calcd. for $IrC_{43}H_{49}P_3NSi_2$: C, 56.07; H, 5.36; N, 1.52. Found: C, 55.80; H, 5.35; N, 1.40. Yield: 0.04 g (76%).

Results and Discussion

Ir(III) Phosphides. The iridium(III) methyl diarylphosphide complexes $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$ (**2a**, R = phenyl; **2b**, R = *m*-tolyl) were synthesized by transmetalation of the previously reported[27] square-pyramidal iridium(III) methyl iodide derivative $Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]$ (1) with stoichiometric amounts of the corresponding lithium diarylphosphide. The reaction proceeds within minutes at room temperature with a

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dramatic color change as the deep green color of the methyl iodide derivative changes to dark purple of the phosphide complex (eq 1). The visible spectra of these complexes show a strong absorption band at 536 nm ($\epsilon = 3.11 \times 10^3$ M^{-1} cm^{-1}), presumably due to a d–d transition, which is characteristic of most five-coordinate d^6 molecules.[27,30–32]

$$\underset{\mathbf{1}}{Ir(CH_3)I[N(SiMe_2CH_2PPh_2)_2]} + LiPR_2 \xrightarrow[(-LiI)]{THF} Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2] \quad [1]$$

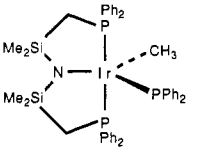
2a R = Ph

2b R = m-tol

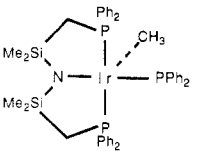
The displacement of the iodide by the phosphide anion is sensitive to steric crowding both at the iridium center and at the phosphide itself. For example, bulkier phosphides such as $LiPPr^i_2$ or $LiP(o\text{-tol})_2$ do not react with the methyl iodide complex **1**; only starting materials are recovered. If the phenyl iodide $Ir(Ph)I[N(SiMe_2CH_2PPh_2)_2]$ or the benzyl iodide $Ir(CH_2Ph)I[N(SiMe_2CH_2PPh_2)_2]$ complexes are employed with $LiPPh_2$, again only starting materials are observed even after extended reaction times. Lithium phenylphosphide, LiPHPh, does react with the methyl iodide complex **1**, but a mixture of products is obtained in which some of the expected product $Ir(CH_3)PHPh[N(SiMe_2CH_2PPh_2)_2]$ can be detected by $^{31}P\{^1H\}$ NMR spectroscopy; however, it is a minor component, and we have been unable to isolate anything from this reaction.

The ^1H NMR spectra of the isolated diarylphosphide complexes **2a** and **2b** are straightforward. An AB quartet of virtual triplets[33] for the PCH_2Si protons in the ligand backbone and wide separation of the ortho and meta/para protons of the phenyl region[34] are typical of a trans orientation of the chelating phosphine donors. The $Si(CH_3)_2$ resonances are observed as two sharp singlets of equal intensity, indicating inequivalent environments above and below the metal tridentate plane, exactly in line with earlier work[27] on five-coordinate complexes stabilized by this ligand system. Again however, the ^1H NMR spectral data do not readily distinguish between the two basic geometries possible for a five-coordinate molecule: trigonal bipyramidal (**tbp**) or square-pyramidal (**sqp**). For the latter case, there is also uncertainity as to which ligand is apical: methyl (**sqp1**), diarylphosphide (**sqp2**), or amide (**sqp3**).

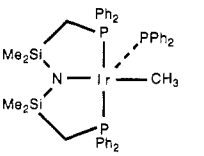
The ^1H NMR spectral data easily rule out the **sqp3** geometry, as the methyl ligand would be expected to be strongly coupled to the trans phosphide and thus resonate as a doublet of triplets (cis coupled to the two phosphines of the ligand and a large coupling from the trans phosphide); in fact, the methyl ligand appears as an approximate quartet, indicating coupling to three cis-oriented phosphorus-31 nuclei. To further distinguish between the remaining stereoisomers, **tbp**, **sqp1**, and **sqp2**, an nOe difference experiment was conducted. Upon irradiation of the downfield methylene proton (PCH_2Si) resonance, a small enhancement of the methyl ($Ir–CH_3$) resonance is observed. However, no enhancement of these methyl protons occurs when the upfield methylene resonance is



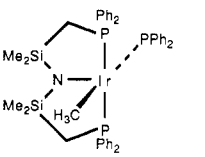
tbp



sqp1



sqp2

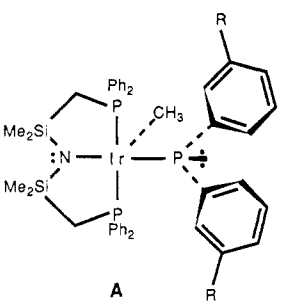


sqp3

irradiated. Therefore, the **sqp2** stereochemistry in which the methyl group is trans to the amide is eliminated since no enhancement should be observed for this stereoisomer regardless of which methylene resonance is irradiated.

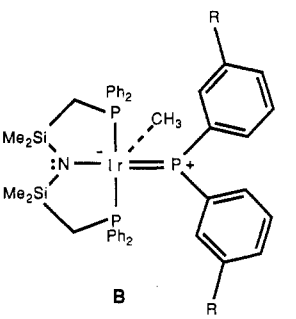
Previous nOe difference type experiments[27] for the **sqp1**-type iridium(III) methyl bromide complex $Ir(CH_3)Br[N(SiMe_2CH_2PPh_2)_2]$ show a fairly large enhancement of the apical methyl protons (approximately 3 times that observed for the methyl protons of **2a**) when the appropriate methylene protons are irradiated; in comparison,[35] the **tbp**-type iridium(III) dimethyl complex $Ir(CH_3)_2[N(SiMe_2CH_2PPh_2)_2]$ displays no enhancement of the methyl resonance on irradiating methylene protons. Thus, the extent of enhancement[36] observed for the methyl protons of the diarylphosphide complexes reported here suggests these species possess a stereochemistry intermediate between the **tbp** and **sqp1** forms; for the purpose of this work **sqp1** form is assumed (vide infra).

One further aspect of the stereochemistry must be addressed. As shown below, the geometry of the terminal phosphide ligand itself in these complexes can either be pyramidal (**A**) or planar (**B**). If the phosphide phosphorus



A

pyramidal



B

planar

were pyramidal, as in **A**, it would have to be freely rotating or locked in a symmetric conformation with respect to the rest of the molecule to account for the observed symmetry in solution. At low temperatures, no loss of symmetry is observed by NMR spectroscopy. In the pyramidal geometry, the iridium center is coordinatively unsaturated (assuming no π-donation from the amido donor of the tridentate ligand) and thus there exists the possibility that a suitable empty orbital on the iridium can overlap with

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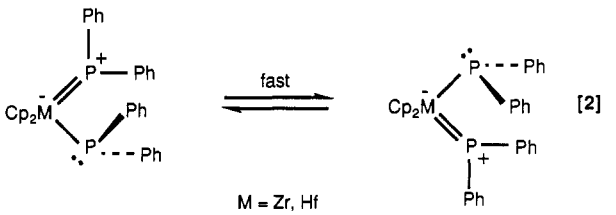
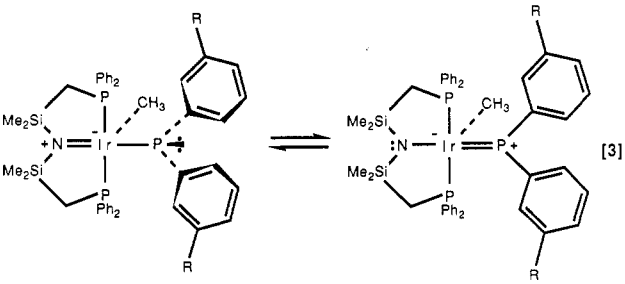
(36) (a) As a reviewer points out, the reduced nOe enhancement may be a result of the lone pair on phosphorus affecting the dipole–dipole, through-space relaxation of the methylene protons. However, the effect of neighboring functional groups such as OMe, OH, or NMe_2, all having lone pairs of electrons, is apparently negligible.[36b] (b) Saunders, K. K.; Easton, J. W. In *Determination of Organic Structures by Physical Methods*; Nachod, F. C., Zuckerman, J. J., Randall, E. W., Eds.; Academic Press: New York, 1976; Vol. 6, p 271.

the filled orbital on phosphorus to generate a planar, multiply bonded phosphenium ligand as in **B**. This planar geometry is also consistent with the solution spectroscopic data. To distinguish these two geometries by $^{31}P\{^1H\}$ NMR spectroscopy is not possible since the observed chemical shifts of the phosphides **2a** and **2b** are in the range 105–120 ppm and is similar to that found[18] for the zirconocene and hafnocene diphenylphosphide complexes $(\eta^5\text{-}C_5H_5)M(PPh_2)_2$ (M = Zr, Hf) which are proposed to be in dynamic equilibrium between the two possible geometries (eq 2).



[2]

An interesting possibility, suggested only by the similar chemical shifts mentioned above, is that both the pyramidal and planar geometries are in dynamic equilibrium assisted by the amide function as shown below (eq 3).

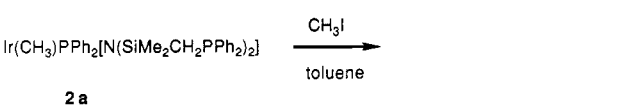


[3]

2 (R = H, Me)

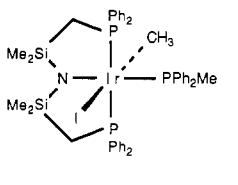
Although we have no direct structural or spectroscopic evidence to support such an equilibrium, interconversion between the two possible geometries should be facile given the precedent[18] of the metallocene derivatives above and the coordinatively unsaturated nature[37] of the iridium center. As will be discussed in the next section, the phosphide unit displays nucleophilic character which is typical[5] of the pyramidal form but not inconsistent with the proposed equilibrium.

Reaction of $Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$ (2a) with Methyl Iodide. The complex $Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$ (**2a**) reacts instantaneously with methyl iodide at room temperature as evidenced by the immediate discharge of the intense purple of the phosphide complex to produce a yellow solution. Workup affords an octahedral iridium(III) methyldiphenylphosphine complex of the formula $Ir(CH_3)I(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$ (**3**) in good isolated yield with no evidence of any other side products (eq 4).

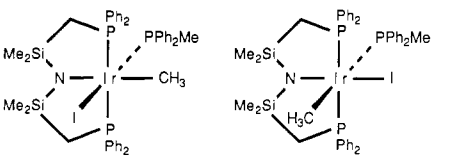


2a **3** [4]

The ^1H and $^{31}P\{^1H\}$ NMR spectra of **3** show that it is stereoisomerically pure. Once again, the presence of virtual coupling for the methylene protons in the ^1H NMR spectrum is consistent with trans phosphine donors of the tridentate ligand, thereby establishing that the ligand is bound in a meridional fashion in the octahedral geometry. Thus, there are only three possible stereoisomers for the structure of this complex in solution: **o1**, **o2**, and **o3**. The

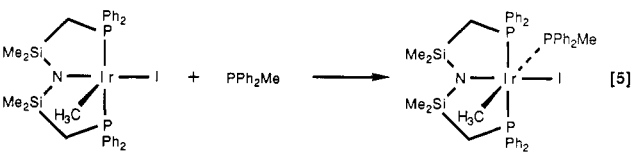


o1



o2 **o3**

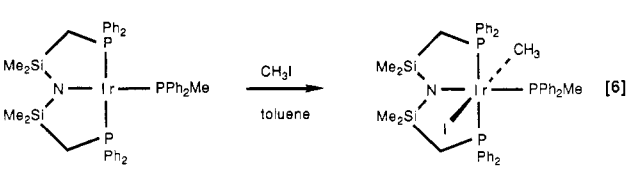
^1H NMR spectral data rule out the isomer **o3**, since the methyl ligand would be expected to resonate as a doublet of triplets for this stereochemistry because of a large trans coupling to the PPh_2Me ligand and a cis coupling to the two phosphine donors of the tridentate ligand; in fact, it is observed to be a four-line pattern. Interestingly, the isomer **o3** was unambiguously prepared by the straightforward addition of PPh_2Me to the coordinatively unsaturated methyl iodide complex **1** (eq 5). The product is isomerically pure and, as mentioned above, has the expected doublet of triplets for the methyl resonance ($^3J_{PPh_2Me,H}$ = 20.0 Hz, $^3J_{CH_2PPh_2,H}$ = 6.0 Hz).



[5]

1 **o3**

A distinction between the isomers **o1** and **o2** was accomplished via an independent experiment. Given that the oxidative addition of alkyl halides proceeds kinetically to generate trans adducts,[38] the reaction between square-planar complex $Ir(PPh_2Me)[N(SiMe_2CH_2PPh_2)_2]$ should result in the formation of isomer **o1** (eq 6). The ^1H NMR spectrum of the product obtained from this reaction was *identical* with that of **3**, which allowed assignment of structure **o1** to **3**.



[6]

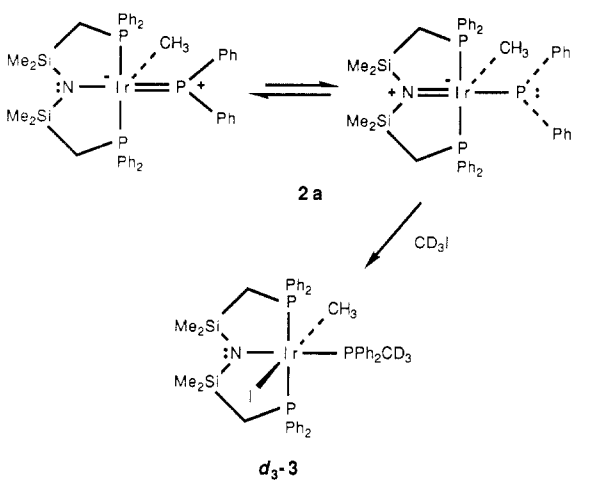
3 = **o1**

In order to discover the source of the methyl group in the methyldiphenylphosphine ligand for complex **3**, the analogous reaction with CD_3I was carried out. The ^1H NMR spectrum for the product **3**-d_3 did not show the doublet at 1.58 ppm (in **3** $^2J_{P,H}$ = 10.6 Hz) as observed for the PPh_2Me ligand in the analogous reaction with CH_3I;

(37) A related pyramidal to planar interconversion has been proposed[9] to occur via Cl^- loss, again emphasizing the important relationship between coordinative unsaturation and the planar form.

(38) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987, p 280.

Scheme I



furthermore, a broad peak centered at the same chemical shift was detected in the $^2H\{^1H\}$ NMR spectrum, which is obviously assigned to the coordinated PPh_2CD_3 moiety. This labeling experiment (Scheme I) shows that the reaction of the phosphide complex **2a** with CH_3I or CD_3I involves intermolecular nucleophilic attack of the phosphide ligand with the electrophile and not prior reductive elimination of the methyl and phosphide ligands followed by oxidative addition.

One further aspect of this intermolecular methylation of the phosphide ligand is the relationship between the stereochemistry of the starting material **2a** and the observed, isomerically pure product **3**. By assuming that the stereochemistry of **2a** is square pyramidal with the methyl group apical (**sqp1**), then approach of the electrophile CH_3I to the open face (trans to the methyl) gives the correct product stereochemistry as **o1**. This stereoselectivity is by no means absolute proof of the stereochemistry for **2a**, but the simplicity of the mechanism and the lack of other octahedral isomers for **3** make such a proposal appealing.

Conclusions

The complexes $Ir(CH_3)PR_2[N(SiMe_2CH_2PPh_2)_2]$ (R = Ph and *m*-tol) contain two potentially basic ligands: the disilylamide donor and the terminal diarylphosphide ligand. However, only the phosphide is nucleophilic toward methyl iodide to stereoselectively generate an octahedral complex, the structure of which can be related to the proposed stereochemistry of the starting phosphide derivative. Although the nucleophilicity of the phosphide ligand is usually associated with a pyramidal geometry at phosphorus, it is possible that the planar and pyramidal geometries are in dynamic equilibrium assisted by the lone pair[39] on the amide nitrogen.

Acknowledgment. Financial support was provided by NSERC of Canada. We gratefully acknowledge the generous loan of $IrCl_3$ from Johnson Matthey.

(39) That the lone pair on the disilylamide nitrogen donor is available for donation and not necessarily delocalized onto silicon d orbitals has been documented in: Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803.

[(1*R*)-1-Acetamido-3-(methylthio)propyl]boronic Acid and the X-ray Structure of Its Ethylene Glycol Ester

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Received July 13, 1988

[(1*R*)-1-Acetamido-3-(methylthio)propyl]boronic acid (**6**), the boronic acid analogue of *N*-acetyl-L-methionine, has been synthesized starting from (*s*)-pinanediol vinylboronate (**1**), and the structure of its ethylene glycol ester (**7**) (a 1,3,2-dioxaborolane) has been determined by X-ray diffraction. Reaction of **1** with (dichloromethyl)lithium yielded the (chloroallyl)boronate **2**, which was converted by lithiohexamethyldisilazane to the silylated amino derivative **3**. Desilylation and acylation of **3** to (acetamidoallyl)boronate **4** was followed by radical addition of methanethiol to form crystalline (*s*)-pinanediol [(1*R*)-1-acetamido-3-(methylthio)propyl]boronate (**5**), which was unsatisfactory for an X-ray structure. Cleavage with boron trichloride yielded the free boronic acid **6**, which formed a crystalline ethylene glycol ester **7**. The X-ray structure shows that the oxygen atom of the acetamido group is coordinated to the weakly acidic boron atom. The five-membered 1,3,2-dioxaborolane ring is nonplanar, in accord with the chiral induction properties of 4,5-disubstituted 2-alkyl-1,3,2-dioxaborolanes in their reactions with (dihalomethyl)lithiums.

α-Amino boronic acids have proved to be surprisingly unstable, though they survive long enough to permit the efficient synthesis of their stable *N*-acyl derivatives.[1-4] Some of these compounds have shown interesting properties as serine protease inhibitors.[1,2,5,6] As part of our program of synthesizing boron analogues of common acylated amino acids, we have prepared the *N*-acetyl-L-methionine analogue **6**. The ethylene glycol ester **7** has provided a satisfactory crystal for an X-ray structure de-

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(4) Matteson, D. S.; Sadhu, K. M. *Organometallics* **1984**, *3*, 614-618.
(5) (a) Kettner, C. A.; Shenvi, A. B. *J. Biol. Chem.* **1984**, *259*, 15106-15114. (b) Soskel, N. T.; Watanabe, S.; Hardie, R.; Shenvi, A. B.; Punt, J. A.; Kettner, C. A. *Am. Rev. Resp. Dis.* **1986**, 635-638, 639-642.
(6) (a) Philipp, M.; Maripuri, S. *FEBS Lett.* **1981**, *133*, 36-38. (b) Philipp, M.; Maripuri, S.; Matteson, D. S.; Jesthi, P. K.; Sadhu, K. M. *Biochemistry* **1983**, *22*, A13.

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