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Reversible Cyclometalation of Silyl Ligands. First X-ray Structure of an Iridium(I) Silyl That Is Not Stabilized by Chelation

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The iridasilacycle *fac*-$(PMe_3)_3Ir(o\text{-}C_6H_4SiMe_2)(H)$ (**1**) results from the ortho metalation of the transient $(PMe_3)_3Ir(SiMe_2Ph)$ (**7**), generated from $Ir(PMe_3)_4Cl$ and $PhMe_2SiLi$ at ambient temperature. Complex **1** can also be obtained from *fac*-$(PMe_3)_3Ir(CH_3)(H)(SiMe_2Ph)$ (**6**), which, when heated, reductively eliminates methane. **1** and its analog *fac*-$(PMe_3)_3Ir(o\text{-}C_6H_4SiPh_2)(H)$ (**2**), react with hydrogen at 80 °C to yield the dihydridosilyliridium(III) complexes *fac*-$(PMe_3)_3Ir(SiR_2Ph)(H)_2$ (**3**, R = Me; **4**, R = Ph). The reaction of **1** with deuterium demonstrates that initial opening of the iridasilacycle takes place, followed by D−D oxidative addition to **7**. The reaction of **1** with CO allows us to trap the iridium(I) species and provides a synthetic route to $Ir(PMe_3)_2(CO)_2(SiMe_2Ph)$ (**5**). Complex **5** was identified by spectroscopy and by X-ray crystallography and was synthesized independently from **3** and CO. The chemistry presented shows that metalation of silyl ligands can be a facile reversible process that takes place under mild conditions. It also indicates that iridasilacycles can be used as a masked form of electron-rich Ir(I) silyl complexes, which are not readily accessible species.

Introduction

Intramolecular activation of ligand C−H bonds leading to the formation of metallacycles is a common reaction of transition-metal complexes.[1] It is well-established for different ligand types such as hydrocarbyls, as well as N-, P-, As-, Sb-, O-, and S-bound ligands.[1] However, there are only a few examples of metallacycles resulting from the metalation of silyl ligands. These, to our knowledge, include $(dcpe)Pt(C_6H_4)Si(SiMe_3)_2$, prepared by Fink and co-workers,[2] *fac*-$(PMe_3)_3Ir(o\text{-}C_6H_4SiPh_2)(H)$ and *fac*-$(PMe_3)_3Ir(CH_2CH_2OSi(OEt)_2)(H)$, which we reported earlier,[3] and *fac*-$(PMe_3)_3Ir(SiMe_2SiMe(SiMe_3)SiMe_2CH_2)(H)$,[4] communicated very recently by Tilley et al. The reactivity of these complexes has been studied very little, the only accessible information being hydrolytic cleavage of the Si−Ph bond in Fink's compound[2] and hydrogen-catalyzed equilibration of the diastereomeric mixture of isomers of Tilley's iridasilacycle.[4] We report here our results on the reversibility of cyclometalation of arylsilyl ligands in (trimethylphosphine)iridium complexes. We show that: (i) this electron-rich system does not require elevated temperatures for the ortho metalation to occur, (ii) reactive $(PMe_3)_3IrSiR_2Ph$ species are available due to C−H reductive elimination which occurs under mild conditions, and (iii) they can be trapped by H_2 or CO. We also report the first X-ray structural characterization of an iridium(I) silyl complex, $Ir(PMe_3)_2(CO)_2(SiMe_2Ph)$, which is not stabilized by chelation. Part of these results has been communicated previously.[5]

Experimental Section

General Considerations. Methods of handling air-sensitive compounds which were employed in this work are described in detail elsewhere.[3b] Deuterium gas (Matheson, 99.9% D) and carbon monoxide (99.9%, from local sources) were used without further purification. $HSiMe_2Ph$ (98%, Aldrich) was degassed by purging with dry N_2 before use. The NMR spectra were measured using a Bruker AMX 400 spectrometer at 400 MHz (^1H), 162 MHz (^{31}P), and 100 MHz (^{13}C) and referenced as described earlier.[3b] ^2H NMR spectra (61.4 MHz) were externally referenced to the signal of C_6D_6 at δ 7.15 ppm. FD-MS spectra were obtained from the Institute of Mass Spectrometry, University of Amsterdam, Amsterdam, The Netherlands. Microanalyses were performed by the Microanalysis Laboratory of The Hebrew University of Jerusalem.

Preparation of *fac*-$(PMe_3)_3Ir(o\text{-}C_6H_4SiMe_2)(H)$ (1). To a stirred suspension of 52 mg (0.098 mmol) of $Ir(PMe_3)_4Cl$[6] in 5.4 mL of THF was dropwise added 0.21 mL of a 0.62 M solution of $Me_2PhSiLi$[7] in THF. The mixture was stirred for 10 min at room temperature, after which the solvent was

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removed under vacuum. The residue that formed was extracted with 5 mL of pentane. The extract after filtration was evacuated to dryness to produce a yellow oily material. The oil was recrystallized from a minimum amount of pentane to yield after 2 days at −20 °C 26 mg (48%) of pure **1** in the form of colorless crystals. Anal. Calcd for $C_{17}H_{38}IrP_3Si$: C, 36.74; H, 6.89. Found: C, 36.97; H, 6.73. FD-MS (Ir-193/191): *m/z* 556/554. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −62.4 (dd with ^{29}Si satellites, $J_1 = 21.3$ Hz, $J_2 = 14.9$ Hz, $^2J_{P-Si,trans} = 127$ Hz, 1P trans to Si); −59.1 (dd, $J_1 = 17.6$ Hz, $J_2 = 14.9$ Hz, 1P trans to C); −55.2 (dd, $J_1 = 21.3$ Hz, $J_2 = 17.7$ Hz, 1P trans to H). ^{1}H NMR (20 °C, C_6D_6): δ −10.32 (d of pseudo t, $^2J_{H-P,trans} = 124.5$ Hz, $^2J_{H-P,cis} = 19.4$ Hz, 1H, Ir−*H*); 0.72 (d, $^4J_{H-P,trans} = 3.0$ Hz, 3H, $Si-CH_3$; the signal of another CH_3 group overlaps with the signal of PMe_3 at δ 1.01 ppm but shifts upfield and is easily observed at 60 °C as a doublet at δ 0.95 ppm ($^4J_{H-P,trans} = 2.5$ Hz, 3H); 1.01 (d, $^2J_{H-P} = 7.4$ Hz, 9H, $P(CH_3)_3$); [1.27 (d, $^2J_{H-P} = 7.1$ Hz, 9H, $P(CH_3)_3$); 1.29 (d, $^2J_{H-P} = 6.8$ Hz, 9H, $P(CH_3)_3$); these two signals appear as a pseudotriplet but are clearly distinguished as two doublets at δ 1.32 and 1.33 ppm at 60 °C]; [7.18 (m), 7.29 (m), 4H, C_6H_4]. $^{13}C\{^1H\}$ NMR ($(CD_3)_2CO$): δ 1.0 (dd, $J_1 = 9.2$ Hz, $J_2 = 1.1$ Hz; $Si-CH_3$); 7.3 (m, $J_1 = 7.3$ Hz, $J_2 = 3.8$ Hz, $J_3 < 1$ Hz, unresolved; $Si-CH_3$); 20.3 (ddd, $J_1 = 27.8$ Hz, $J_2 = 5.8$ Hz, $J_3 = 3.0$ Hz; $P(CH_3)_3$); 23.5 (dt, $J_d = 22.6$ Hz, $J_t = 2.9$ Hz; $P(CH_3)_3$); 25.0 (ddd, $J_1 = 29.3$ Hz, $J_2 = 5.0$ Hz, $J_3 = 3.5$ Hz; $P(CH_3)_3$); [119.1 (br), 126.1 (br), 127.0 (br), 134.6 (br), 137.6 (ddd, $J_1 = 84.2$ Hz, $J_2 = 10.2$ Hz, $J_3 = 7.6$ Hz), 168.9 (dt, $J_t = 10.7$ Hz, $J_d = 2.2$ Hz); C_6H_4].

Preparation of *fac*-$(PMe_3)_3Ir(SiMe_2Ph)(H)_2$ (3). To a solution of 35 mg (0.07 mmol) of $HIr(PMe_3)_4$[8] in 2 mL of benzene was added 11.5 μL (0.075 mmol) of $HSiMe_2Ph$. The yellow solution was left overnight at room temperature, after which it became colorless. The solvent was removed under vacuum to yield 43 mg (90%) of pure **3** as a waxy white solid. Anal. Calcd for $C_{17}H_{40}P_3SiIr$: C, 36.61; H, 7.23. Found: C, 36.54, H, 7.48. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −61.7 (t with ^{29}Si satellites, $J = 20.4$ Hz, $^2J_{P-Si,trans} = 128$ Hz, 1P trans to Si); −57.4 (d, $J = 20.4$ Hz, 2P trans to H). ^{1}H NMR (C_6D_6): δ −12.22 (symmetrical second-order m, $J_1 = 95.5$ Hz, $J_2 = 20.3$ Hz, 2H; Ir−*H*); 0.99 (d, $^4J_{H-P,trans} = 2.3$ Hz, 6H; $Si(CH_3)_2$; 1.19 (d, $^2J_{H-P} = 7.4$ Hz, 18H; $2P(CH_3)_3$, trans to H); 1.26 (d, $^2J_{H-P} = 7.6$ Hz, 9H; $P(CH_3)_3$, trans to Si); [7.20 (tt, $J_1 = 7.3$ Hz, $J_2 = 1.3$ Hz, $1H_{para}$), 7.38 (t, $J = 7.4$ Hz, $2H_{meta}$), 8.08 (m, $2H_{ortho}$); $Si-C_6H_5$].

Preparation of *fac*-$(PMe_3)_3Ir(CH_3)(H)(SiMe_2Ph)$ (6). This complex was prepared in complete analogy with its triethyl-, triphenyl-, and triethoxysilyl analogs, for which we reported full characterization data, including X-ray crystal structures of the first two of them.[3] **6** was isolated from its benzene solution in quantitative yield as a white powder. FD-MS (Ir-193/191): *m/z* 572/570. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −63.4 (dd with ^{29}Si satellites, $J_1 = 20.5$ Hz, $J_2 = 17.6$ Hz, $^2J_{P-Si,trans} = 153$ Hz, 1P trans to Si); −58.9 (pseudo t, $J = 17.4$ Hz, 1P trans to CH_3); −58.5 (dd, $J_1 = 20.5$ Hz, $J_2 = 17.2$ Hz, 1P trans to H). ^{1}H NMR (C_6D_6): δ −11.91 (d of pseudo t, $^2J_{H-P,trans} = 135.3$ Hz, $^2J_{H-P,cis} = 19.4$ Hz, 1H, Ir−*H*); 0.26 (m, $^3J_{H-H} = 1.1$ Hz, 3H, $Ir-CH_3$); 0.85 (d, $^4J_{H-P,trans} = 1.7$ Hz, 3H, $Si-CH_3$); 0.88 (d, $^4J_{H-P,trans} = 2.4$ Hz, 3H, another $Si-CH_3$); 1.09 (d, $^2J_{H-P} = 7.0$ Hz, 18H; $2P(CH_3)_3$, coincidence); 1.11 (d, $^2J_{H-P} = 7.4$ Hz, 9H; $P(CH_3)_3$); [7.21 (tt, $J_1 = 7.3$ Hz, $J_2 = 1.4$ Hz, $1H_{para}$), 7.37 (t, $J = 7.5$ Hz, $2H_{meta}$), 8.07 (m, $2H_{ortho}$); $Si-C_6H_5$].

Thermolysis of 6. A solution of 12 mg (0.02 mmol) of **6** in 0.5 mL of C_6D_6 was heated in a screw-capped NMR tube at 95 °C in an oil bath. $^{31}P\{^1H\}$ and ^{1}H NMR spectra of the reaction mixture were periodically checked to show complete disappearance of the starting material after 2 days. The resulting mixture contained ~70% of **1**, ~15% of **3**, and ~15% of *mer,trans*-$(PMe_3)_3Ir(C_6D_5)_2(D)$ (**10**), which were identified by their NMR spectra. The ^{1}H NMR spectrum exhibited also signals due to CH_4 (δ 0.15 ppm), $(CH_3)_3SiPh$ (δ 0.19 ppm), and CH_3D (δ 0.14 ppm, 1:1:1 triplet with $J = 2$ Hz). $^{31}P\{^1H\}$ NMR of **10** (C_6D_6): δ −45.4 (d of pseudo t, $^2J_{P-P,cis} = 20.3$ Hz, $^2J_{P-D,cis} = 3.1$ Hz, 2P, mutually trans), −54.4 (t of pseudo t, $^2J_{P-P,cis} = 20.3$ Hz, $^2J_{P-D,trans} = 22.3$ Hz, 1P trans to D). The ^{1}H NMR of **10** is essentially the same as that reported[3] for its nondeuterated isotopomer, except for the absence of the signals due to the hydride and the C_6H_5 groups.

Reaction of 1 and 2 with H_2. Solutions of **1** and **2** (0.01 mmol) in C_6D_6 (0.4 mL) were pressurized with 80 psi of hydrogen in a high-pressure 5 mm NMR tube. The tubes were placed in an oil bath and were heated at 80 °C for 20 h (**1**) or 40 h (**2**), after which quantitative formation of **3** and **4** respectively was detected by $^{31}P\{^1H\}$ and ^{1}H NMR.

Reaction of 1 with D_2. This reaction was carried out completely analogously to the reaction of **1** with H_2. Characterization of **3-D_2**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −61.7 (m, 1P trans to Si), −57.4 (m, 2P trans to D); ^{1}H NMR is the same as for **3**, except for the absence of the multiplet at δ −12.22 due to the hydrides; $^2H\{^1H\}$ NMR (C_6H_6) δ −12.2 (br symmetrical m, $J_1 = 14.4$ Hz, $J_2 = 3.2$ Hz, Ir−*D*).

Reaction of 1 with CO. Formation of $Ir(PMe_3)_2(CO)_2(SiMe_2Ph)$ (5). A solution of **1** (0.02 mmol) in C_6D_6 (0.4 mL) was pressurized with 40 psi of CO in a high-pressure 5 mm NMR tube. The tube was heated in an oil bath at 85 °C for 40 h, after which $^{31}P\{^1H\}$, ^{1}H, and $^{13}C\{^1H\}$ NMR indicated quantitative formation of **5** and liberation of 1 equiv of PMe_3. The solvent was removed under vacuum to afford **5** as a colorless solid in essentially quantitative yield. Colorless needles suitable for X-ray analysis were obtained by slow evaporation of a concentrated pentane solution of **5** at room temperature. FD-MS (Ir-193/191): *m/z* 536/534. IR (film): ν_{CO} (cm^{-1}) = 1896 vs, 1905 s, 1932 sh, 1945 vs. $^{31}P\{^1H\}$ NMR (C_6D_6): δ −64.6 (s with ^{29}Si satellites, $^2J_{P-Si} = 30.5$ Hz). ^{1}H NMR (C_6D_6): δ 1.06 (second-order pseudo d, $J = 8.3$ Hz, 18H; $2P(CH_3)_3$), 1.13 (t, $^4J_{H-P} = 1.1$ Hz, 6H; $Si(CH_3)_2$), [7.18 (m, $1H_{para}$), 7.32 (t, $J = 7.5$ Hz, $2H_{meta}$), 8.03 (m, $2H_{ortho}$); $Si-C_6H_5$]. $^{13}C\{^1H\}$ NMR (C_6D_6): δ 8.05 (t, $J = 3.8$ Hz; $Si(CH_3)_2$); 23.16 (symmetrical six-line pattern of X part of an ABX spin system; $2P(CH_3)_3$); [127.57 (s), 127.59 (s), 134.55 (s), the fourth signal was not found; $Si-C_6H_5$], 188.57 (t, $^2J_{C-P} = 5.5$ Hz; Ir−*C*O).

Reaction of 3 with CO. The procedure and amounts were exactly the same as for the reaction of **1** with CO. The reaction was much slower and less selective. The $^{31}P\{^1H\}$ and ^{1}H NMR spectra were periodically checked to show after 312 h, when the reaction was interrupted, that the reaction mixture contained 67% of **5**, 18% of $(PMe_3)_2Ir(CO)_2(H)$ (**8**), and 9% of $(PMe_3)_2Ir(CO)(H)_2(SiMe_2Ph)$ (**9**), along with 6% of unreacted **3**. Complexes **8** and **9** were tentatively assigned on the basis of the following signals in the NMR spectra. **8**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −62.0 (br s); ^{1}H NMR (C_6D_6) δ -11.31 (t, $^2J_{H-P,cis} = 28.4$ Hz, 1H, Ir−*H*). **9**: $^{31}P\{^1H\}$ NMR (C_6D_6) δ −62.6 (d, $J = 21$ Hz, 1P), −60.2 (d, $J = 21$ Hz, 1P); ^{1}H NMR (C_6D_6) δ -10.9 (d of br m, $^2J_{H-P,trans} \approx 111$ Hz, $^2J_{H-P,cis} \approx 22$ Hz, 1H, Ir−*H*), −10.46 (symmetrical five-line m (in fact, ddd), $^2J_{H-P,cis} = 23$ Hz, $^2J_{H-P,cis} = 19$ Hz, $^2J_{H-H,cis} = 4$ Hz, 1H, Ir−*H*).

X-ray Crystallographic Analysis of 5. The structure of compound **5** was determined using a Rigaku AFC5R four-circle diffractometer with Mo Kα radiation (graphite monochromator; $\lambda = 0.710\ 73$ Å). Unit cell dimensions were determined from 25 reflections. Details of crystal parameters and data collection are given in Table 1. Three standards were collected 19 times each with a 4% change of intensity. The structure was solved by the Patterson method (SHELXS-92[9a]) and refined using full-matrix least-squares refinement based on F^2 (SHELXL-93[9b]). The data were not corrected for absorption. Hydrogens were calculated from a difference Fourier map and refined in a riding mode. For 207 parameters and 3384 data with no restraints, the following final discrepancy factors were obtained: R1 = 0.0360 (based on F^2), wR2 = 0.0577 ($I > 2\sigma(I)$); R1′ = 0.0923, wR2′ = 0.0751 (all data); GOF (on F^2) =

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[8] Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580.

[9] (a) Sheldrick, G. M. SHELXS92, Program for crystal structure solution; University of Göttingen, Göttingen, Germany, 1992. (b) Sheldrick, G. M. SHELXL93, Program for crystal structure refinement; University of Göttingen, Göttingen, Germany, 1993.

Table 1. Crystallographic Parameters for the Structure of 5

empirical formula	$C_{16}H_{29}O_2P_2SiIr$
formula mass	535.62
color and habit	colorless needles
cryst size	0.2 × 0.2 × 0.4
cryst system	monoclinic
space group	$P2_1/c$ (No.14)
a, Å	10.456(2)
b, Å	8.104(2)
c, Å	25.028(3)
β, deg	100.10(3)
V, Å^3	2087.9(8)
Z	4
d(calcd), g/cm^3	1.704
μ, mm^{-1}	6.609
diffractometer	Rigaku AFC5R
radiation (wavelength, Å)	Mo Kα (λ = 0.710 73)
monochromator	graphite
temp, K	110
mode	ω
θ_{max}, deg	27.53
scan speed, deg/min	8
scan width, deg	1.2
collcn range	$-13 \leq h \leq -3$, $0 \leq k \leq 10$, $-29 \leq l \leq 32$
no. of reflcns	
collcd	3445
indepdt	3389
no. of variables	207
$R1$	0.0360
w$R2$	0.0570

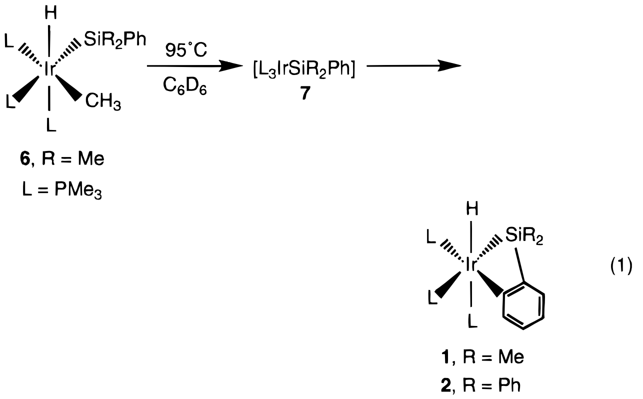
Table 2. Selected Interatomic Bond Lengths (Å) in a Molecule of 5

Ir(1)−C(10)	1.873(10)	P(3)−C(33)	1.806(11)
Ir(1)−C(11)	1.887(10)	P(3)−C(31)	1.829(9)
Ir(1)−P(3)	2.340(3)	P(3)−C(32)	1.831(7)
Ir(1)−P(4)	2.353(2)	P(4)−C(42)	1.794(12)
Ir(1)−Si(2)	2.442(3)	P(4)−C(43)	1.801(11)
Si(2)−C(27)	1.863(12)	P(4)−C(41)	1.798(10)
Si(2)−C(21)	1.890(10)	O(10)−C(10)	1.149(11)
Si(2)−C(28)	1.890(10)	O(11)−C(11)	1.146(12)

1.042. The largest residual peak and hole had values of 0.875 and −0.958 e Å^{-3}. Selected interatomic bond lengths and angles are presented in Tables 2 and 3.

Results and Discussion

Synthesis of Iridasilacycle 1. The compound *fac*-$(PMe_3)_3\overline{Ir(o\text{-}C_6H_4Si}Me_2)(H)$ (**1**) can be obtained in two different ways. The first one is completely analogous to the synthesis which we reported for its analog **2**[3] (eq 1). When complex **6**, which has a methyl, a hydride, and a dimethylphenylsilyl group in mutually cis positions, is heated to 95 °C for 2 days, C−H reductive elimination occurs. It leads to the intermediate $(PMe_3)_3Ir(SiMe_2Ph)$ (**7**; not observed), which ortho-metalates to produce **1**. However, this route is complicated by the competitive C−Si and H−Si reductive eliminations,[3] which lead to the formation of about 30% of undesired products (see Experimental Section for details). Still, crude **1** can be recrystallized from cold pentane and obtained pure.



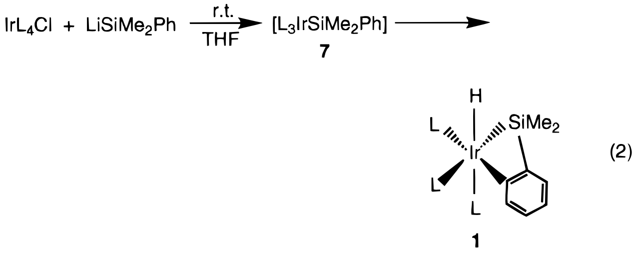
6, R = Me
L = PMe$_3$

1, R = Me
2, R = Ph

Table 3. Selected Bond Angles (deg) in a Molecule of 5

C(10)−Ir(1)−C(11)	137.0(5)	C(10)−Ir(1)−Si(2)	84.7(2)
C(10)−Ir(1)−P(3)	112.4(3)	C(11)−Ir(1)−Si(2)	84.8(2)
C(11)−Ir(1)−P(3)	109.9(3)	P(3)−Ir(1)−Si(2)	94.25(10)
C(10)−Ir(1)−P(4)	88.5(2)	P(4)−Ir(1)−Si(2)	166.91(10)
C(11)−Ir(1)−P(4)	92.8(2)	O(10)−C(10)−Ir(1)	178.0(9)
P(3)−Ir(1)−P(4)	98.67(7)	O(11)−C(11)−Ir(1)	177.7(11)

A better way to obtain **1** involves a nucleophilic attack of (dimethylphenylsilyl)lithium at $Ir(PMe_3)_4Cl$ (eq 2).



This reaction presumably generates the intermediate **7** at room temperature in THF.[10] Removal of the solvent under vacuum followed by the pentane workup affords pure **1** in the form of colorless crystals.

The composition and stereochemistry of **1** were elucidated from its ^{31}P, ^{1}H, and ^{13}C NMR spectra and FD-MS and microanalysis data. Three doublets of doublets (one of them having ^{29}Si satellites[11]) in the $^{31}P\{^1H\}$ NMR spectrum together with appropriately split signals in ^{1}H and $^{13}C\{^1H\}$ NMR spectra indicate facial arrangement of the PMe_3 ligands in the complex. The octahedral coordination around the iridium center is completed by the silicon, the ortho-metalated aryl fragment, and the hydride, which gives rise in the ^{1}H NMR spectrum to a widely spaced doublet of triplets at δ −10.32 ppm. Importantly, such a stereochemistry makes the two silicon-bound methyl groups inequivalent, as clearly seen in ^{1}H (doublets at δ 0.72 and 1.02 ppm) and $^{13}C\{^1H\}$ (doublet of doublets at δ 1.0 and a multiplet at 7.3 ppm) NMR spectra. As expected, once the rigid silametallacycle is formed, the six carbons of the aromatic ring become chemically and magnetically inequivalent as well and give rise to six signals in the $^{13}C\{^1H\}$ NMR spectrum. The signal due to the metalated carbon atom appears at δ 137.6 ppm as a doublet of doublets of doublets with a large $^2J_{C-P,trans}$ value of 84.2 Hz and two different small $^2J_{C-P,cis}$ values of 10.2 and 7.6 Hz.

The facility of the ortho metalation that leads to **1** is noteworthy. It clearly indicates that the heating used in the synthesis of **1** from **6** is necessary not for the intramolecular C−H activation of the dimethylphenylsilyl group in **7** but, rather, for inducing reductive elimination of methane from **6**. We note that an analogous metalation (preceded by a series of rear-

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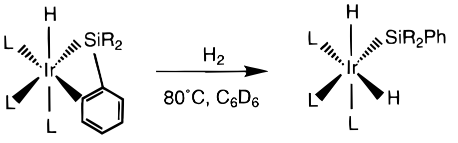
[10] The analogous reaction of $Rh(PMe_3)_4Cl$ leads to the stable *nonmetalated* Rh(I) analog of **7**, namely $(PMe_3)_3Rh(SiMe_2Ph)$; see: Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359.

[11] For the range of coupling constants $^2J_{P-Si,cis}$ and $^2J_{P-Si,trans}$ see, for example: (a) Ozawa, F.; Hikida, T.; Hayashi, T. *J. Am. Chem. Soc.* **1994**, *116*, 2844. (b) Zarate, E. A.; Kennedy, V. O.; McCune, J. A.; Simons, R. S.; Tessier, C. A. *Organometallics* **1995**, *14*, 1802.

rangements) of an *aliphatic* C−H bond of the tris(trimethylsilyl)silyl ligand at the same $(PMe_3)_3Ir$ center was also shown to proceed at ambient and even lower temperatures.[4]

Reactivity of Complexes 1 and 2. (a) Reactions with H_2 and D_2. The iridasilacycles **1** and **2** are easily isolable, very stable compounds. They are not sensitive to air and moisture in the solid state. Moreover, complex **1** remains unchanged after prolonged (several days) heating at 100−110 °C in cyclohexane. However, these silametallacycles react with hydrogen. When benzene solutions of **1** or **2** are placed under 80 psi of hydrogen at 80 °C, the dihydridosilyliridium(III) complexes **3** and **4** are quantitatively formed (eq 3). Complex **4** is known. It was synthesized from $HIr(PMe_3)_4$ and $HSiPh_3$ and was characterized by spectroscopy and by X-ray crystallography.[11b] For the purposes of identification, complex **3** was synthesized independently using a completely analogous reaction of $HIr(PMe_3)_4$ with $HSiPhMe_2$ and was fully characterized.

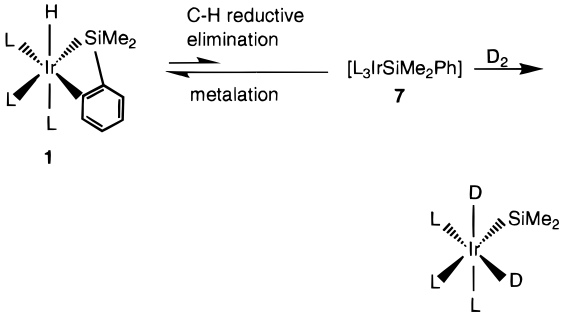


(3)

1, R = Me
2, R = Ph

3, R = Me
4, R = Ph

Formation of the dihydrides **3** and **4** from the silacycles **1** and **2** may be rationalized in two ways. The first one invokes C−H reductive elimination, i.e., opening of the cycle, with subsequent H−H oxidative addition to the intermediate **7** (path A). The second one involves H−H oxidative addition, i.e., formation of an Ir(V) intermediate, prior to the opening of the cycle (path B). Iridium(V) complexes with hydrides and silyls as ligands are not very common but are known.[12] On the other hand, very electron-rich octahedral complexes of Ir(III) with tightly bound small ancillary ligands, like the ones described herein, seem not to be very well suited for very facile reductive eliminations,[3] which would result in the formation of Ir(I) species. This mechanistic dilemma was resolved by using deuterium instead of hydrogen. If the *silacycle first opens up* and deuterium adds to the resulting Ir(I), then nonlabeled $Si-C_6H_5$ and iridium *dideuteride* would be formed. If the D−D oxidative addition *precedes* the C−H reductive-elimination step, then one would expect *scrambling* of the deuterium label between the ortho position of the aromatic ring and the iridium hydrides. The latter case requires also that there should be no fast secondary exchange between deuterium gas and the dihydridosilyliridium complex.[13] Examination of $^{31}P\{^1H\}$, ^1H, and $^2H\{^1H\}$ NMR spectra of the product of the reaction between **1** and D_2 unequivocally demonstrated that path A is operative and the dideuteridosilyl species **3-D₂** is formed (eq 4).



1

7

3-D2

(4)

This conclusion is based on the following observations. (1) The $^{31}P\{^1H\}$ NMR spectrum of the product exhibited two broad, heavily distorted multiplets due to $^2H-^{31}P$ couplings. Their chemical shift values exactly match those of the non-deuterated **3**. (2) In the ^1H NMR spectrum signals of the ortho protons of the phenyl ring at δ 8.08 ppm were not affected with respect to both the line shape and integrated intensity. At the same time the signal due to the hydrides at δ −12.22 ppm was negligible. (3) The $^2H\{^1H\}$ NMR spectrum showed essentially no incorporation of the deuterium label into the ortho positions of the phenyl ring, while a broad symmetrical multiplet appeared at δ −12.2 ppm. Its chemical shift as well as the apparent coupling constants (J_1 = 14.4, J_2 = 3.2 Hz) fit those expected for the dideuteride **3-D₂**. (4) The reaction between **3** and D_2 carried out under exactly the same conditions did not result in any appreciable $Ir-(H)_2/D_2$ exchange. After 20 h at 80 °C the signals of **3** at δ −61.7 and −57.4 ppm in the $^{31}P\{^1H\}$ NMR spectrum remained a sharp triplet and doublet, respectively, the signal at δ −12.22 ppm in the ^1H NMR spectrum due to the hydrides did not diminish in integration, and the intensity of Ir-D signals in the $^2H\{^1H\}$ NMR spectrum was negligible.

The described facility of C-H reductive elimination leading to the opening of the iridasilacycles **1** and **2** is somewhat surprising. For example, it is known that the closely related complex *fac*-$(PMe_3)_3\overline{Ir(CH_2C(CH_3)_2C}H_2)$, which has a four-membered Ir−C−C−C ring, is extremely stable.[14] It is nonreactive with C_6D_6 at 90 °C and with CO at moderate pressures[14a] and survives when heated at 150 °C for days.[14b] The difference between this complex, on one hand, and complexes **1** and **2**, on the other, is even more striking, since in the former only sp³ carbons are involved in metalation. Activation of C−H bonds of these carbons is expected to be both kinetically and thermodynamically *less favorable* than that of sp² carbons of **1** and **2**. Still, the metalation of $(PMe_3)_3Ir(CH_2E(CH_3)_3)$ (E = C, Si) is essentially irreversible up to 80 °C,[15] while **1** and **2** are quite reactive at this temperature. It was noted that an increase of steric bulk at a tris(phosphine)iridium center can facilitate both cyclometalation and opening of metallacycles. The latter was also associated with the strain relief of the four-membered ring.[14,15] We believe that **1** and **2** (as well as their precursors) are not extremely sterically congested. Their four-membered rings include silicon which is larger in volume than carbon, probably resulting in less strain. Thus, the reasons for the easy C−H reductive eliminations

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[12] (a) Fernandez, M.-J.; Maitlis, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2063. (b) Tanke, R. S.; Crabtree, R. H. *Organometallics* **1991**, *10*, 415. (c) Loza, M.; Faller, J. W.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 2937. (d) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodriguez, L. *Organometallics* **1996**, *15*, 823.

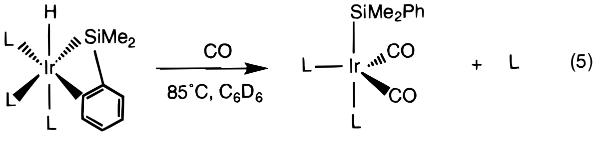
[13] For example, $Ir(H)_2(Et_3Si)(CO)(dppe)$ was reported to undergo 75% exchange of hydrides with D_2 at 60 °C over 24 h: Hays, M. K.; Eisenberg, R. *Inorg. Chem.* **1991**, *30*, 2623.

[14] (a) Tulip, T. H.; Thorn, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 2448. (b) Calabrese, J. C.; Colton, M. C.; Herskovitz, T.; Klabunde, U.; Parshall, G. W.; Thorn, D.; Tulip, T. H. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 302.

[15] Harper, T. G. P.; Desrosiers, P. J.; Flood, T. C. *Organometallics* **1990**, *9*, 2523.

that **1** and **2** undergo remain unclear and may have to do with an electronic effect of the silyl group.

(b) Reaction of 1 with CO. Formation of the Ir–SiMe$_2$Ph Complex 5. To make use of the above described ability of **1** to open up, generating the transient iridium(I) silyl intermediate **7**, we carried out the reaction of **1** with carbon monoxide with the hope of obtaining a *stable* Ir(I) silyl complex. We note that there are very few reported examples of isolated silyl complexes of iridium(I).[16] Subjecting a benzene solution of **1** to 40 psi of CO gas at 85 °C in a high-pressure NMR tube resulted in liberation of 1 equiv of PMe$_3$ and quantitative formation of bis(phosphine)dicarbonyl(dimethylphenylsilyl)iridium(I) (**5**) as the sole organometallic product (eq 5). It was identified using IR and NMR spectroscopy, and its structure was verified by X-ray diffraction.



(5)

1 **5**

Complex **5** exhibits in $^{31}P\{^1H\}$ NMR a sharp singlet resonance with ^{29}Si satellites at δ −64.6 ppm which remains sharp even at −70 °C. Since the $P(CH_3)_3$ protons do not give rise in ^1H NMR to a virtual triplet signal,[17] this is indicative of a very fast intramolecular dynamic process which equilibrates the two phosphines. The ^{31}P chemical shift value is typical for other saturated 5-coordinate Ir(I) trimethylphosphine complexes. The ^{29}Si satellites indicate the presence of a silyl ligand bound to the iridium center. The value of $^2J_{P-Si} = 30.5$ Hz is much smaller than the ones observed for rigid hexacoordinate Ir(III) complexes with the same silyl ligand (compare $^2J_{P-Si,trans} = 127$ Hz for **1**, 128 Hz for **3**, and 153 Hz for **6**). This may be a result of **5** being in solution a fluxional molecule without a permanent trans arrangement of the silyl and one phosphine ligand. There is only one signal in the carbonyl region of $^{13}C\{^1H\}$ NMR of **5** at δ 188.57. It is split into a triplet with $^2J_{C-P} = 5.5$ Hz, indicating again the apparent equivalence of the two phosphorus nuclei. The IR spectrum exhibits two strong bands for the coordinated carbonyl groups with ν_{CO} values of 1896 and 1945 cm^{-1} (the former is additionally split at its top into two bands, while the latter has a shoulder at 1932 cm^{-1}). This definitely rules out a structure with a single carbonyl ligand as well as a configuration with two carbonyls arranged trans to each other. The final proof for the structure of **5** was obtained from an X-ray crystallographic analysis (see below).

Alternative Route to 5. Having synthesized **5** from **1**, one would suppose that **5** could also be formed in a formally analogous reaction of H–H reductive elimination from **3** under a CO atmosphere. Indeed, this reaction is feasible, but under the same conditions it is much slower and less selective than reaction of **1** with CO. The kinetic followup by $^{31}P\{^1H\}$ NMR of the disappearance of **3** is given in Figure 1. It is first order in [**3**] with $k_{obs} = 9.18 \times 10^{-3}$ h^{-1} ($R = 0.999$). After 312 h of monitoring by NMR the reaction was interrupted, resulting in a mixture of 67% of **5**, 6% of unchanged **3**, and two other products which on the basis of their NMR signals were tentatively assigned as $(PMe_3)_2Ir(CO)_2(H)$ (**8**; 18%) and $(PMe_3)_2Ir(CO)(H)_2(SiMe_2Ph)$ (**9**; 9%) (Figure 1b). Free PMe$_3$, H$_2$, and HSiMe$_2$Ph were detected in ^{31}P and ^1H NMR. These results together with the lack of exchange between **3** and D$_2$ imply that H–H and H–Si reductive eliminations from **3** *do not occur* under the conditions studied. Only after predissociation of one of the tightly bound PMe$_3$ ligands from **3** and CO coordination can these reactions take place (leading to **5** and **8**), the overall process being much slower than the corresponding reactions of the iridasilacycles **1** and **2**.

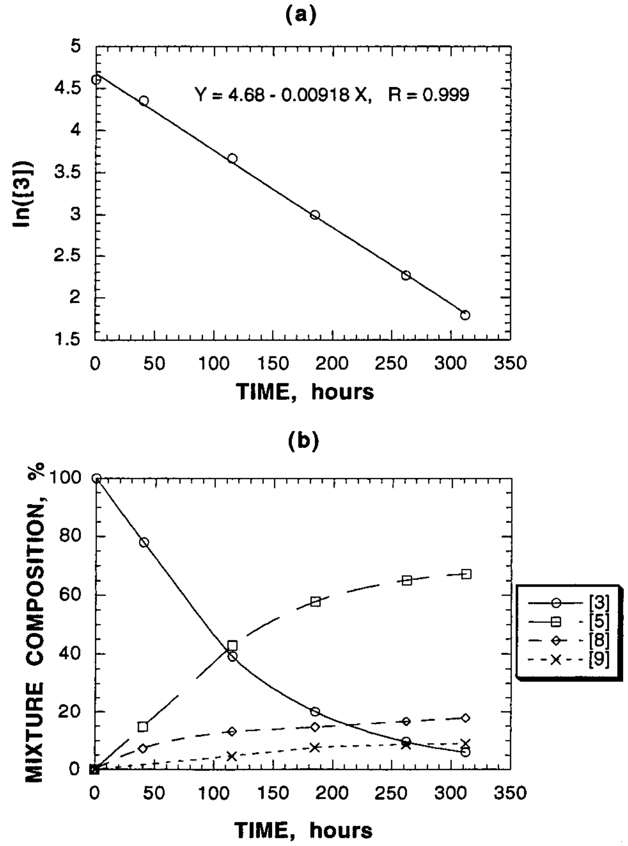
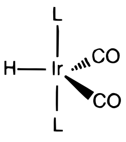


Figure 1. Kinetic followup of the reaction of **3** (0.05 M) with 40 psi of CO in C$_6$D$_6$ at 85 °C: (a) plot of ln([**3**]) versus time; (b) plots of [**3**], [**5**], [**8**], and [**9**] versus time.



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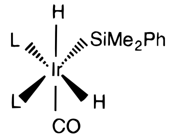

9

Description of the Structure of 5. Slow evaporation of a concentrated pentane solution of **5** yielded colorless needles suitable for an X-ray crystallographic study. A perspective view of the solid-state structure of **5** is presented in Figure 2. As seen from Figure 2 and from Tables 2 and 3, the coordination geometry around the iridium center is trigonal bipyramidal with the silyl and one of the phosphine ligands in the axial positions, the second phosphine and two carbonyls

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[16] (a) Auburn, M. J.; Grundy, S. L.; Stobart, S. R.; Zaworotko, M. *J. Am. Chem. Soc.* **1985**, *107*, 266. (b) Esteruelas, M. A.; Lahoz, F. J.; Oliván, M.; Oñate, E.; Oro, L. A. *Organometallics* **1994**, *13*, 4246.

[17] The closely related Rh analog of **5**, namely Rh(PMe$_3$)$_2$(CO)$_2$(SiPh$_3$), is known. According to its ^1H NMR the $P(CH_3)_3$ ligands are mutually trans and give rise to a virtual triplet. See: Thorn, D. L.; Harlow, R. L. *Inorg. Chem.* **1990**, *29*, 2019.

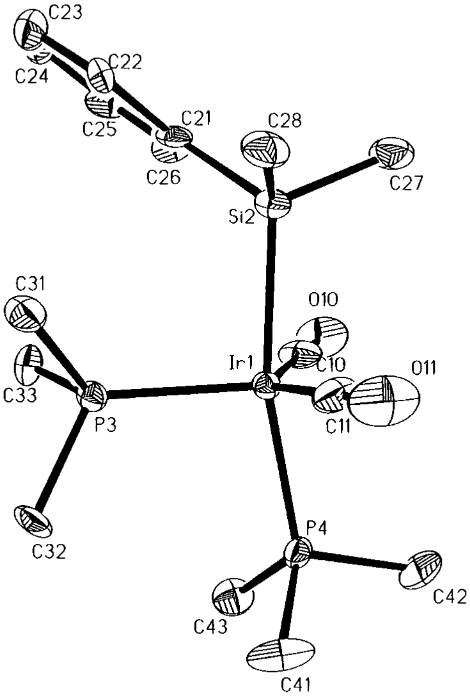

Figure 2. Perspective view of the coordination geometry of **5**. Hydrogen atoms are omitted for clarity.

occupying three equatorial sites. Although in the solid-state structure of **5** the two phosphines are cis to each other and are obviously different, such a molecule is expected to be stereochemically nonrigid in solution, which results in the NMR spectral data described above. There are several important features of the structure of **5**. It is worthy of note that the arrangement of the ligands is the same as that reported by Stobart for the chelate-stabilized complex $[\overline{\mathrm{Ir}(\mathrm{PPh_2CH_2CH_2Si}}\mathrm{Me_2})(\mathrm{PPh_3})(\mathrm{CO})_2]$.[16a] The Ir–Si distance of 2.442(2) Å is long. It is longer than typical Ir–Si bonds in Ir(III) complexes, both octahedral and pentacoordinate,[18] as well as those in seven-coordinate Ir(V) silyls.[12c] The aforementioned compound of Stobart has a long Ir–Si bond as well (2.454(6) Å[16a]). The anchoring of the silyl ligand in it results in an almost linear arrangement of $\mathrm{P_{trans}}$–Ir–Si (the corresponding angle has a value of 175.7(2)°[16a]), while in **5** the P(4)–Ir(1)–Si(2) angle equals 166.91(10)°. This may decrease the degree to which the trans influence of the phosphorus is transmitted, leading to a shorter Ir–Si bond. To our knowledge, **5** is the second Ir(I) silyl to be structurally characterized. It is the first structure of an Ir(I) silyl that is not stabilized by chelation.

Chemical Properties of 5. One would expect that **5**, if capable of ligand dissociation in solution, should be quite reactive in oxidative-addition processes, as is the case for other Ir(I)–trimethylphosphine complexes. We were quite surprised to find out that a cyclopentane solution of **5** is not sensitive to either atmosperic oxygen or moisture. Moreover, a 30-fold excess of MeI did not react with **5** in cyclopentane over 1 day. When **5** is produced from **1**, it coexists in solution with 1 equiv of free $\mathrm{PMe_3}$ for prolonged periods of time at elevated temperatures and exhibits no reactivity. Hydrogen does not add to **5** as well. For a comparison, related square-planar bis(trimethylphosphine) complexes of Ir(I) that have only one CO ligand, such as *trans*-$(\mathrm{PMe_3})_2\mathrm{Ir(CO)X}$ (X = Cl, $\mathrm{CH_3}$, Ph), all rapidly add $\mathrm{H_2}$ at room temperature and 1 atm, resulting in the corresponding dihydrides.[19] Cis-phosphine analogs (dppe)Ir(CO)X[20] and (dfepe)Ir(CO)H[21] do so as well. Importantly, even the coordinatively saturated $(\mathrm{PCy_3})\mathrm{Ir(CO)_3(SiPh_3)}$, (dfepe)-$\mathrm{Ir(CO)_2(H)}$, and $(\mathrm{PMe_3})_2\mathrm{Ir(CO)_2Cl}$, which have phosphines or another ligand of lower σ-donating capacity, readily lose one CO in solution[16b,21,22] and are, therefore, capable of reacting with $\mathrm{H_2}$. The observed lack of reactivity of **5** is undoubtedly a consequence of its retaining the saturated 18-electron structure in solution. The synergism between the very strong σ-donor capability of both $\mathrm{PMe_3}$ and $\mathrm{SiMe_2Ph}$ groups and the π-acceptor character of CO ligands results in the very high stability of **5** with respect to ligand dissociation and, hence, in its inertness in oxidative-addition reactions.[23]

Conclusions

In this paper we have presented an example of metalation of a silyl ligand which occurs at the $(\mathrm{PMe_3})_3$-Ir center under very mild conditions. Moreover, we have provided the first conclusive demonstration of reversibility of such a process. In contrast to the very well-established reversal of metalation of phosphine ligands,[24] this reaction was unknown for silyls. We have also described synthetic ways to, and measured the X-ray structure of, a coordinatively saturated Ir(I) silyl complex not stabilized by chelation, which is remarkable in its stability with respect to ligand dissociation. We continue to explore possible ways of synthesizing coordinatively unsaturated iridium(I) silyls. We also continue investigating the chemistry of such complexes generated in situ.

Acknowledgment. We thank Dr. Linda J. W. Shimon of the X-ray diffraction facility of the Weizmann Institute for solving the crystal structure of **5**. This work was supported by the US-Israel Binational Science Foundation, Jerusalem, Israel. M.A. thanks The Clore Foundations, Jerusalem, Israel, for a scholarship. D.M. is the holder of the Israel Matz Professorial Chair of Organic Chemistry.

Supporting Information Available: Tables of atomic coordinates, bond distances and angles, and anisotropic displacement parameters for all non-hydrogen atoms and hydrogen atom coordinates for **5** (5 pages). Ordering information is given on any current masthead page.

OM960214I

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[18] Information on Ir–Si bond lengths in five- and six-coordinate complexes of Ir(III) can be found in: (a) Tilley, T. D. In *The Silicon-Heteroatom Bond*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1991; pp 264, 343. (b) Goikhman, R.; Aizenberg, M.; Kraatz, H.-B.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865. See also refs 3b, 11d, and 12.

[19] Burk, M. J.; McGrath, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034.

[20] Deutsch, P. P.; Eisenberg, R. *Chem. Rev.* **1988**, *88*, 1147 and references therein.

[21] Schnabel, R. C.; Carroll, P. S.; Roddick, D. M. *Organometallics* **1996**, *15*, 655.

[22] Burk, M. J.; Crabtree, R. H. *Inorg. Chem.* **1986**, *25*, 931.

[23] Relevant to our observations is the reported facile reductive elimination of $\mathrm{H_2}$ from $\mathrm{IrH_3(CO)(PEt_2Ph)_2}$ under a CO atmosphere, which leads to the similarly stabilized 18-electron species $\mathrm{IrH(CO)_2(PEt_2Ph)_2}$. See: Mann, B. E.; Masters, C.; Shaw, B. L. *J. Chem. Soc. D* **1970**, 846.

[24] Bennett, M. A.; Milner, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6983.