626-62-0; CH_3I, 74-88-4; CH_2Cl_2, 75-09-2; CH_3OH, 67-56-1; CF_3CO_2H, 76-05-1; C_2H_5OH, 64-17-5; CH_3CO_2H, 64-19-7; $CH_3CH_2CH_2OH$, 71-23-8; $(CH_3)_2CHOH$, 67-63-0; H_2O, 7732-18-5; PMe_2Ph, 672-66-2; THF, 109-99-9.

Supplementary Material Available: Tables of elemental analyses, melting points, molecular weights, and IR data [ν(CO), ν(IrCl)] (4 pages). Ordering information is given on any current masthead page.

Secondary to Normal Alkyl Group Rearrangements in Octahedral Iridium(III) Complexes. 2. Bis(organo) Derivatives

Martin A. Bennett* and Geoffrey T. Crisp

Research School of Chemistry, Australian National University, G.P.O. Box 4, Canberra A.C.T. 2601, Australia

Received October 9, 1985

Organoiridium(I) complexes $IrR'(CO)(PMe_3)_2$ [R′ = Me (**1**), CH_2SiMe_3 (**2**), and Ph (**3**)] have been made by reaction of the appropriate alkyllithium R′Li with $IrCl(CO)(PMe_3)_2$. The methyl derivative **1** oxidatively adds primary or secondary alkyl bromides or iodides RX to give octahedral bis(organo)iridium(III) complexes $IrXMeR(CO)(PMe_3)_2$ [R = $CH_2CH_2CH_3$, $CH(CH_3)_2$, $CH_2CH_2CH_2CH_3$, $CH(CH_3)CH_2CH_3$, $CH_2[CH_2]_3CH_3$, $CH(CH_3)CH_2CH_2CH_3$]. The (trimethylsilyl)methyl (**2**) and phenyl (**3**) derivatives oxidatively add primary or secondary alkyl iodides RI, but not bromides, to give similar complexes $IrIR'R(CO)(PMe_3)_2$. In all cases the stereochemistry of oxidative addition is trans and the PMe_3 ligands are mutually trans. The *sec*-alkyl complexes $IrXR'$-*sec*-$R(CO)(PMe_3)_2$ rearrange to the corresponding *n*-alkyl isomers $IrXR'$-*n*-$R(CO)(PMe_3)_2$ in benzene/methanol at room temperature. The rearrangement is quantitative for R′ = Me or Ph, but in the case of R′ = CH_2SiMe_3 it is accompanied by reductive elimination, giving $IrI(CO)(PMe_3)_2$, olefin (propene or butene from R = $CH(CH_3)_2$ or $CH(CH_3)CH_2CH_3$, respectively), and $(CH_3)_4Si$. The alkyl rearrangement is probably initiated by reversible, methanol-promoted dissociation of halide ion trans to the *sec*-alkyl group. This is followed by rapid, reversible β-hydride elimination and stereospecific return of halide ion trans to the rearranged alkyl group. When R′ = Me or CH_2SiMe_3, an intermediate containing cis PMe_3 ligands can be detected as isomerization proceeds, probably *cis*-$IrXR'$-*n*-$R(CO)(PMe_3)_2$; however, it is not established with certainty whether the alkyl group in the intermediate is normal or secondary.

In the preceding paper,[1] we showed that *sec*-alkyliridium(III) complexes $IrClI$-*sec*-$R(CO)L_2$ (L = PMe_3, PMe_2Ph), formed by oxidative addition of *sec*-alkyl iodides to $IrCl(CO)L_2$, isomerize cleanly to the thermodynamically more stable *n*-alkyl compounds in the presence of protic solvents such as methanol, water, or trifluoroacetic acid. Alkyl- and aryliridium(I) complexes of the type $IrR(CO)L_2$[2,3] should be more electron-rich than $IrCl(CO)L_2$ and could be expected to oxidatively add alkyl halides, provided the σ-bonded group is not too bulky. The addition of hydrogen halides (HX) to $Ir(aryl)(CO)(PPh_3)_2$ to give iridium(III) hydrido aryls $IrHX(aryl)(CO)(PPh_3)_2$ is well-known,[4] but at the start of our work the only example of addition of an alkyl halide was the reaction of methyl iodide with $Ir(C_6F_5)(CO)(PPh_3)_2$ to give $IrIMe(C_6F_5)(CO)(PPh_3)_2$.[5] When this paper was about to be submitted, a report of the preparation of $IrMe(CO)(PPh_3)_2$ and its reaction with methyl iodide to give $IrIMe_2(CO)(PPh_3)_2$ appeared.[6] Related dimethyliridium(III) complexes $IrXMe_2L_3$ (X = Cl, I; L = PMe_2Ph, $AsMe_2Ph$) have been prepared by halogen cleavage of one of the Ir–Me bonds of the trimethyliridium(III) complexes *fac*-$IrMe_3L_3$; the latter are made by reaction of *mer*-$IrCl_3L_3$ with an excess of methylmagnesium chloride.[7] We were interested to see whether a range of bis(alkyl)iridium(III) complexes could be made by the oxidative addition procedure and whether the added alkyl group also would undergo secondary to normal rearrangement. Because $IrCl(CO)(PMe_3)_2$ adds alkyl halides much more readily than does $IrCl(CO)(PPh_3)_2$, we have used as precursors alkyliridium(I) complexes containing trimethylphosphine.

Results

Organoiridium(I) Complexes and Their Reactions with Alkyl Halides. Addition of 1 equiv of methyllithium, [(trimethylsilyl)methyl]lithium, or phenyllithium to $IrCl(CO)(PMe_3)_2$ in toluene at −78 °C gives the corresponding organoiridium(I) complexes $IrR'(CO)(PMe_3)_2$ in yields of 47% (R′ = Me, **1**), 58% (R′ = CH_2SiMe_3, **2**), and 86% (R′ = Ph, **3**), respectively. They are yellow, thermally stable, highly air-sensitive solids which are very soluble in hydrocarbons; they can be recrystallized from hexane. The method of preparation is general, since addition of [(trimethylsilyl)methyl]lithium to $IrCl(CO)L_2$ (L = PPh_3, PMe_2Ph) gives the expected products $Ir(CH_2SiMe_3)(CO)L_2$ which have been identified by their NMR spectra (see Experimental Section).

In the preparation of $IrMe(CO)(PMe_3)_2$ it is important to use just 1 mol of methyllithium/mol of $IrCl(CO)(PMe_3)_2$. Use of 2 mol of methyllithium gives a brown,

---

[1] Bennett, M. A.; Crisp, G. T. *Organometallics*, preceding paper in this issue.

[2] Dickson, R. S. *Organometallic Chemistry of Rhodium and Iridium*; Academic: New York, 1983; Chapter 7, p 275.

[3] Leigh, G. J.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, Sir G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 5, p 541.

[4] Dahlenburg, L.; Nast R. *J. Organomet. Chem.* **1976**, *100*, 395.

[5] Jordan, B. F.; Harris, A. H.; Nainan, K. C.; Sears, C. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1451.

[6] Rees, W. M.; Churchill, M. R.; Li, Y.-Ji.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162.

[7] Shaw, B. L.; Smithies, A. C. *J. Chem. Soc. A* **1967**, 1047.

0276-7333/86/2305-1800$01.50/0

Table I. IR Data (cm^{-1}) for Bis(alkyl)iridium(III) Complexes $IrXRR'(CO)(PMe_3)_2$

	ν(CO) (Nujol)	ν(CO) (CH_2Cl_2)	ν(IrBr)
4a	1995	1995	158
4b	2000	2005	154
4c	2005, 1990	1995	160
4d	2000	1995	167
4e	1994	1995	160
4f	2005	2000	165, 156
5a	2005	1995	
5b	2000	1995	
5d	2000	nm	
12a	2000	2000	
12b	2000	2000	
12c	1995	2000	
12d	1997, 1993	2000	
13a	2010	2020	
13b	2000	2020	
13c	2020, 2000	2020	
13d	2020	2020	

hexane-insoluble residue after evaporation of solvent, and this decomposes rapidly on addition of benzene. The brown solid may contain an anionic species $[IrMe_2(CO)(PMe_3)_2]^-$, but this has not been investigated further.

The IR spectra of **1**–**3** show a single ν(CO) band in the region 1935–1940 cm^{-1} similar to that observed for the aryls $Ir(aryl)(CO)(PPh_3)_2$.[2-4] The frequency is ca. 20 cm^{-1} lower than that for $IrCl(CO)(PMe_3)_2$, as expected if the electron density on the metal atom in the alkyls and aryls is greater than that in the chloro complex. The P–Me resonance in the ^1H NMR spectra of **1**–**3** is a triplet ($^2J_{PH} + {^4J_{PH}} = 8$ Hz), consistent with a mutually trans arrangement of the PMe_3 ligands, and this is confirmed by the observation of a singlet in the $^{31}P\{^1H\}$ NMR spectra at δ_P −20 to −25. In complex **1**, the Ir–Me resonance is a triplet at δ 0.50 ($^3J_{PH}$ = 10 Hz), and in **2** the CH_2SiMe_3 resonance is also a triplet [δ 0.44 ($^3J_{PH}$ = 14 Hz)]. There was no evidence for the formation of cis isomers of **1**–**3**, although such compounds have been isolated when both the σ-bonded group and the tertiary phosphine are bulky, e.g., $Ir(2,4,6\text{-}C_6H_2Me_3)(CO)(PPh_3)_2$.[8] Replacement of PPh_3 in the latter compound by smaller tertiary phosphines gives only the trans isomer.[9]

The methyl complex **1** reacts with alkyl iodides or bromides, but not with chlorides, at ambient temperature in benzene to give bis(alkyl)iridium(III) complexes **4a**–**f** and **5a**–**d**, respectively, in 60–70% yield (eq 1). In these

$$IrMe(CO)(PMe_3)_2 + RX \rightarrow IrXMeR(CO)(PMe_3)_2 \qquad (1)$$

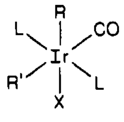
$X = Br$; $R = CH_2CH_2CH_3$ (**4a**), $CH(CH_3)_2$ (**4b**), $CH_2CH_2CH_2CH_3$ (**4c**), $CH(CH_3)CH_2CH_3$ (**4d**), $CH_2[CH_2]_3CH_3$ (**4e**), $CH(CH_3)CH_2CH_2CH_3$ (**4f**)

$X = I$; $R = CH_2CH_2CH_3$ (**5a**), $CH(CH_3)_2$ (**5b**), $CH_2CH_2CH_2CH_3$ (**5c**), $CH(CH_3)CH_2CH_3$ (**5d**)

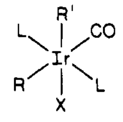
reactions, and in the corresponding additions to **2** and **3** described below, both the organoiridium(I) complex and the alkyl halide must be carefully prepurified (see Experimental Section); otherwise large amounts of byproducts, probably $IrX_2R(CO)(PMe_3)_2$ and $IrX_3(CO)(PMe_3)_2$, are obtained.

Complexes **4a**–**f** and **5a**–**d** are colorless, crystalline solids that can be recrystallized from hexane. They are air-stable both in the solid state and in solution, and their alkyl groups show no tendency to undergo reductive elimination at room temperature. Their IR spectra (Table I) show a single, strong ν(CO) band at ca. 2000 cm^{-1}, and complexes **4a**–**f** show a ν(IrBr) band in the range 154–167 cm^{-1}. The triplet P–Me resonance in the ^1H NMR spectra of all the complexes [except the *sec*-butyl derivative **4d** (see below)] is indicative of mutually trans PMe_3 ligands, and these give rise to a singlet in the $^{31}P\{^1H\}$ NMR spectra (Table II). However, this information does not distinguish between the possible structures **6**, **7**, and **8** (R′ = Me), and, although correlations of ν(IrCl) with the nature of the trans ligand in octahedral iridium(III) complexes are well-established,[7,10,11] there are no similar correlations involving ν(IrBr).

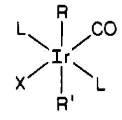
To gain more information, we have measured the far-IR spectra of the model compounds **9**–**11** obtained by trans addition of a methyl halide CH_3X to the appropriate iridium(I) complex $IrY(CO)(PMe_3)_2$ [X = I, Y = Br (**9**); X = Y = Br (**10**); X = Br, Y = Cl (**11**)]. The ν(IrBr) bands appear at 192 cm^{-1} in **9** (Br trans to CO), at 168 cm^{-1} in **11** (Br trans to CH_3), and at 192 and 168 cm^{-1} in **10** (Br trans to CO and Br trans to CH_3, respectively). The spectrum of **11** also shows a ν(IrCl) band at 300 cm^{-1}, as expected for Cl trans to CO. These data indicate that complexes **4a**–**f** do not have Br trans to CO (i.e., structure **8** is excluded), and since alkyl halides almost always add in a trans manner to d^8 complexes, we conclude that complexes **4a**–**f** and **5a**–**d** have structure **6**.



6

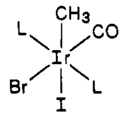


7

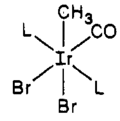


8

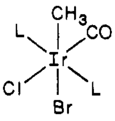
L = PMe_3; X = Br, I; R′ = Me, CH_2SiMe_3, Ph; R = various alkyl groups



9



10



11

In the ^1H NMR spectra of the *sec*-butyl complexes **4d** and **5d** the P–Me resonance appears as a five-line multiplet which collapses to two singlets on ^{31}P decoupling. This demonstrates the inequivalence of the PMe_3 ligands resulting from the chiral center at the secondary alkyl group. This inequivalence was not evident in the $^{31}P\{^1H\}$ NMR spectra of **4d** or **5d**, which are just singlets. Neither ^1H nor ^{31}P NMR spectra of the 1-methylbutyl complex **4f** gave evidence for the expected inequivalence of its PMe_3 ligands.

The Ir–Me resonance in the ^1H NMR spectra of **4a**–**f** and **5a**–**d** is a triplet ($^3J_{PH} \sim$ 8–9 Hz) whose chemical shift depends on the nature of the other alkyl group. Thus, for the *sec*-alkyl complexes **4b**, **4d**, and **4f**, δ(IrMe) is at 0.60, whereas for the *n*-alkyl complexes **4a**, **4c**, and **4e** it appears at 0.40. Also, the ^{31}P chemical shifts of the *sec*-alkyl complexes are ca. 1 ppm to lower frequency than those of the corresponding *n*-alkyls, as was found too in the monoalkyl complexes $IrClIR(CO)L_2$.[1]

The [(trimethylsilyl)methyl]- and phenyliridium(I) complexes **2** and **3**, respectively, react with alkyl iodides in benzene at room temperature to give bis(alkyl)iridium(III) complexes **12a**–**d** and **13a**–**d**, respectively, as colorless solids in 70–80% yield (eq 2). There is no reaction with

---

(8) Mirzali, F.; Dahlenburg, L. *J. Organomet. Chem.* **1979**, *173*, 325. Dahlenburg, L.; von Deuten, K.; Kopf, J. *Ibid.* **1981**, *216*, 113.

(9) Dahlenburg, L.; Sinnwell, V.; Thoennes, D. *Chem. Ber.* **1978**, *111*, 3367.

(10) Bennett, M. A.; Clark, R. J. H.; Milner, D. L. *Inorg. Chem.* **1967**, *6*, 1647.

(11) Shaw, B. L.; Smithies, A. C. *J. Chem. Soc. A* **1968**, 2784.

alkyl chlorides or alkyl bromides under these conditions.

$$\mathrm{IrR'(CO)(PMe_3)_2 + RI \rightarrow IrIRR'(CO)(PMe_3)_2} \quad (2)$$

$R' = CH_2SiMe_3$; $R = CH_2CH_2CH_3$ (**12a**), $CH(CH_3)_2$ (**12b**), $CH_2CH_2CH_2CH_3$ (**12c**), $CH(CH_3)CH_2CH_3$ (**12d**)

$R' = Ph$; $R = CH_2CH_2CH_3$ (**13a**), $CH(CH_3)_2$ (**13b**), $CH_2CH_2CH_2CH_3$ (**13c**), $CH(CH_3)CH_2CH_3$ (**13d**)

The (trimethylsilyl)methyl *sec*-alkyl complexes **12b** and **12d** are air-sensitive and thermally unstable, but they can be stored under nitrogen for a few weeks; the other complexes are air-stable as solids and in solution. The NMR spectroscopic data suggest that **12a–d** and **13a–d** probably have the ligand arrangement shown in **6** ($R' = CH_2SiMe_3$, Ph; X = I) arising from trans addition of the organic iodides to **2** and **3**. The P–Me resonance appears as the usual triplet ($^2J_{PH} + {}^4J_{PH} = 8$ Hz) in the ^{1}H NMR spectra of all except the *sec*-butyl complexes **12d** and **13d** which, like **4d** and **5d**, contain a chiral center at the added carbon atom. In these cases, the P–Me resonances are multiplets (actually two pairs of doublets with a "filled in" triplet), which simplify to two singlets in the ^{1}H{^{31}P} NMR spectrum. The ^{31}P{^{1}H} NMR spectrum of **12d** is just a singlet, despite the inequivalence of the PMe_3 ligands, but that of the phenyl *sec*-butyl complex **13d** is an AB quartet with $^2J_{PP} = 378$ Hz, a value expected for mutually trans tertiary phosphine ligands in octahedral iridium(III) complexes.[12] As usual, the ^{31}P nuclei of the *sec*-alkyl complexes are more shielded (by ca. 4 ppm) than those of the corresponding *n*-alkyl compounds.

The ^{1}H NMR spectra of the CH_2SiMe_3 complexes show some strange effects. In the *sec*-alkyls **12b** and **12d** the triplet due to CH_2SiMe_3 appears at δ 0.06, above the singlet at δ 0.50 due to CH_2SiMe_3, whereas in the corresponding *n*-alkyls **12a** and **12c** the CH_2SiMe_3 protons appear in the range δ 0.33–0.39 and CH_2SiMe_3 is at δ 0.33. In the alkyl chain Ir–C(1)–C(2)–C(3)–C(4) of the phenyl *n*-alkyl complexes **13a** and **13c**, the chemical shifts of the protons on C(1) and C(2) are ca. 0.3–0.6 ppm larger than those of the corresponding protons in the methyl *n*-alkyl complexes **5a** and **5c** and (trimethylsilyl)methyl *n*-alkyl complexes **12a** and **12c**. This suggests that the protons on C(1) and C(2) in **13a** and **13c** are in the deshielding zone of the σ-phenyl group.

Alkyl Group Rearrangement. The *sec*-alkyl methyl complexes $IrXMe\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (X = Br, **4b**; X = I, **5b**) and $IrXMe\{CH(CH_3)CH_2CH_3\}(CO)(PMe_3)_2$ (X = Br, **4d**; X = I, **5d**) undergo quantitative rearrangement at room temperature in benzene–methanol to the corresponding *n*-alkyl methyl complexes $IrXMe(CH_2CH_2CH_3)(CO)(PMe_3)_2$ (X = Br, **4a**; X = I, **5a**) and $IrXMe(CH_2CH_2CH_2CH_3)(CO)(PMe_3)_2$ (X = Br, **4c**; X = I, **5c**), respectively. As with the $IrClIR(CO)(PMe_3)_2$ compounds,[1] there is no isomerization at room temperature in the absence of methanol and the process is accelerated by increasing the proportion of methanol. For example, the time required for complete isomerization of **4b** and **5b** to **4a** and **5a** at room temperature is reduced from 24 h in benzene–methanol (6:1 v/v) to 1 h in benzene–methanol (1:1 v/v). The change with time of the 100-MHz ^{1}H NMR spectrum of the isopropyl complex **4b** in C_6D_6–CD_3OD (4:1 v/v) at 29 °C is shown in Figure 1. After 2 h there are many overlapping resonances (spectrum B), but with the

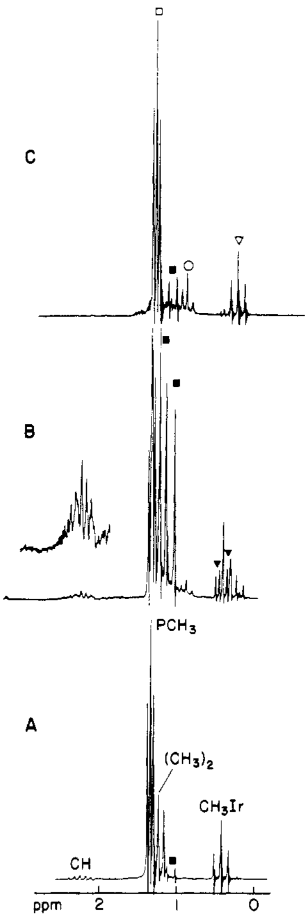


Figure 1. ^{1}H NMR spectra of $IrBrMe\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**4b**) in C_6D_6–CD_3OD (4:1 v/v) at 0.5 h(A), 2.0 h(B), and 24 h(C), showing formation of an intermediate containing cis PMe_3 ligands during isomrization to $IrBrMe(CH_2CH_2CH_3)(CO)(PMe_3)_2$ (**4a**): ■, PCH_3 resonances of intermediate; ▼, $IrCH_3$ resonances of intermediate; □, PCH_3 resonances of **4a**; ○, $IrCH_2CH_2CH_3$ resonances of **4a**; ▽, $IrCH_3$ resonances of **4a**.

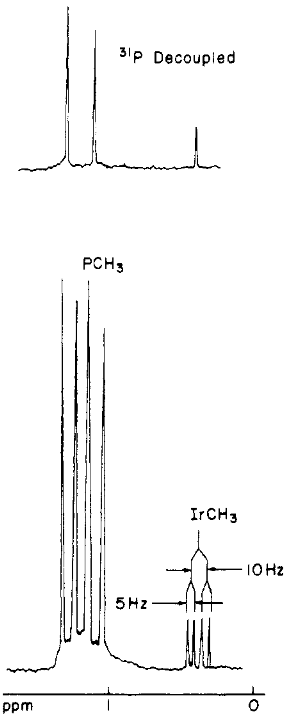


Figure 2. ^{1}H NMR spectrum of intermediate containing cis PMe_3 ligands formed during isomerization of $IrBrMe\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**4b**) to $IrBrMe(CH_2CH_2CH_3)(CO)(PMe_3)_2$ (**4a**) in C_6D_6–CD_3OD (4:1 v/v) at 29 °C.

---

[12] Pregosin, P.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: Berlin, 1979; p 124. (a) The quantity $^2J_{PH} + {}^4J_{PH}$ refers to the doublet separation when the PMe_3 ligands are cis ($^2J_{PP}$ small) and to the separation of the outer lines of the approximate 1:2:1 triplet when the PMe_3 ligands are trans ($^2J_{PP}$ large): Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

Table II. ^1H and $^{31}P\{^1H\}$ NMR Spectra of Bis(alkyl)iridium(III) Complexes $IrXRR'(CO)(PMe_3)_2$[a]

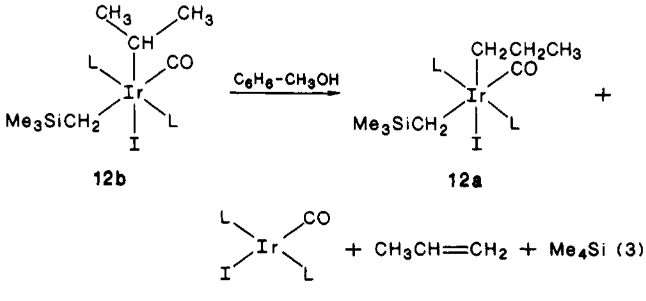
	X	R	R′	δ(PMe)[b]	δ(R′)[c]	δ(R)	δ(P)
4a	Br	$CH_2CH_2CH_3$	CH_3	1.31 (t)	0.40 (t, 9)	1.30 (m, $CH_2CH_2C\mathit{H}_3$), 1.00 (m, $C\mathit{H}_2C\mathit{H}_2CH_3$)	−45.5
4b	Br	$CH(CH_3)_2$	CH_3	1.40 (t)	0.60 (t, 9)	2.32 (sp, J_{HH} = 6 Hz, $C\mathit{H}(CH_3)_2$, 1.36 (d, J_{HH} = 6 Hz, $CH(C\mathit{H}_3)_2$	−46.4
4c	Br	$CH_2CH_2CH_2CH_3$	CH_3	1.32 (t)	0.42 (t, 9)	1.40–0.94 (m, $CH_2CH_2CH_2CH_3$)	−45.6
4d	Br	$CH(CH_3)CH_2CH_3$	CH_3	1.38, 1.37 (m)[d]	0.60 (t, 9)	2.14–1.44 (m, $C\mathit{H}(CH_3)C\mathit{H}_2CH_3$), 1.31 (d, J_{HH} = 7 Hz, $CHC\mathit{H}_3$), 0.99 (t, J_{HH} = 7 Hz, $CH_2C\mathit{H}_3$)	−47.0
4e	Br	$CH_2[CH_2]_3CH_3$	CH_3	1.34 (t)	0.42 (t, 9)	1.40–0.94 (m, $[C\mathit{H}_2]_4C\mathit{H}_3$)	−45.5
4f	Br	$CH(CH_3)CH_2CH_2CH_3$	CH_3	1.20 (t)	0.60 (t, 9)	2.04–1.44 (m, $C\mathit{H}(CH_3)C\mathit{H}_2CH_2CH_3$), 1.30 (d, J_{HH} = 7 Hz, $CH(C\mathit{H}_3)$, 1.01 (m, $CH(CH_3)C\mathit{H}_2C\mathit{H}_3$	nm
5a	I	$CH_2CH_2CH_3$	CH_3	1.42 (t)	0.49 (t, 9)	1.40–1.00 (m, $C\mathit{H}_2C\mathit{H}_2CH_3$), 1.02 (t, J_{HH} = 8 Hz, $CH_2CH_2C\mathit{H}_3$)	−50.9
5b	I	$CH(CH_3)_2$	CH_3	1.48 (t)	0.66 (t, 9)	2.46 (sp, $C\mathit{H}(CH_3)_2$), 1.35 (d, J_{HH} = 7 Hz, $CH(C\mathit{H}_3)_2$)	−51.7
5c	I	$CH_2CH_2CH_2CH_3$	CH_3	1.42 (t)	0.50 (t, 9)	1.5–1.0 (m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2$), 1.04 (t, J_{HH} = 6 Hz, $CH_2CH_2CH_2C\mathit{H}_3$)	−50.8
5d	I	$CH(CH_3)CH_2CH_3$	CH_3	1.39, 1.38 (m)[d]	0.56 (t, 9)	2.04 (m, $C\mathit{H}(CH_3)$), 1.64 (m, $CH(CH_3)C\mathit{H}_2CH_3$), 1.22 (d, J_{HH} = 7 Hz, $CH(C\mathit{H}_3)$), 0.92 (t, J_{HH} = 7 Hz, $CH_2C\mathit{H}_3$)	−51.8
12a	I	$CH_2CH_2CH_3$	CH_2SiMe_3	1.49 (t)	0.33 (t, 10, $C\mathit{H}_2SiMe_3$), 0.33 (s, $CH_2Si\mathit{Me}_3$)	1.40 (m, $C\mathit{H}_2CH_2CH_3$), 1.02 (m, $CH_2C\mathit{H}_2CH_3$)	−50.3
12b	I	$CH(CH_3)_2$	CH_2SiMe_3	1.52 (t)	0.50 (s, $CH_2Si\mathit{Me}_3$), 0.07 (t, 10, $C\mathit{H}_2SiMe_3$)	1.98 (sp, $C\mathit{H}(CH_3)_2$), 1.36 (d, J_{HH} = 7 Hz, $CH(C\mathit{H}_3)_2$	−54.7
12c	I	$CH_2CH_2CH_2CH_3$	CH_2SiMe_3	1.48 (t)	0.39 (t, 10, $C\mathit{H}_2SiMe_3$), 0.33 (s, $CH_2Si\mathit{Me}_3$)	1.40–0.88 (m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_3$)	−52.5
12d	I	$CH(CH_3)CH_2CH_3$	CH_2SiMe_3	1.54, 1.52 (m)[d]	0.48 (s, $CH_2Si\mathit{Me}_3$), 0.06 (t, 10, $C\mathit{H}_2SiMe_3$)	2.0–1.3 (m, $C\mathit{H}(CH_3)C\mathit{H}_2CH_3$), 1.34 (d, J_{HH} = 7 Hz, $CH(C\mathit{H}_3)CH_2CH_3$, 0.96 (t, J_{HH} = 7 Hz, $CH(CH_3)CH_2C\mathit{H}_3$)	nm
13a	I	$CH_2CH_2CH_3$	C_6H_5	1.23 (t)	7.5–7.0 (m)	1.70 (m, $C\mathit{H}_2C\mathit{H}_2CH_3$), 1.12 (m, $CH_2CH_2C\mathit{H}_3$)	−50.0
13b	I	$CH(CH_3)_2$	C_6H_5	1.36 (t)	7.5–7.0 (m)	2.48 (sp, $C\mathit{H}(CH_3)_2$), 1.50 (d, J_{HH} = 6 Hz, $CH(C\mathit{H}_3)_2$)	−51.7
13c	I	$CH_2CH_2CH_2CH_3$	C_6H_5	1.24 (t)	7.5–7.0 (m)	1.74–1.44 (m, $C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$) 1.08 (m, $CH_2CH_2CH_2C\mathit{H}_3$)	−50.4
13d	I	$CH(CH_3)CH_2CH_3$	C_6H_5	1.38, 1.37 (m)[d]	7.5–7.0 (m)	2.30–1.94 (m, $C\mathit{H}(CH_3)C\mathit{H}_2CH_3$), 1.47 (d, J_{HH} = 7 Hz, $CH(C\mathit{H}_3)$), 1.06 (t, J_{HH} = 7 Hz, $CH_2C\mathit{H}_3$)	−51.8, −51.7[e]

[a] ^1H NMR spectra in C_6D_6 at 29 °C with internal Me_4Si, $^{31}P\{^1H\}$ NMR spectra in C_6H_6 at 35 °C; ^{31}P chemical shifts are positive to high frequency of external 85% H_3PO_4. [b] Virtual triplet, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, except where stated. [c] Coupling constant in parentheses refers to $^3J_{PH}$. [d] Simplifies to two singlets on ^{31}P decoupling. [e] AB quartet, $^2J_{PP}$ = 378 Hz.

aid of ^{31}P decoupling these can be satisfactorily assigned to **4b**, **4a**, and an intermediate that is present only during the isomerization. The ^1H NMR spectrum of this intermediate is obtained by subtracting the resonances due to **4a** and **4b** from spectrum B and is shown in Figure 2. It contains a pair of P–Me doublets at δ 1.31 ($^2J_{PH} + {}^4J_{PH}$ = 9 Hz) and 1.12 ($^2J_{PH} + {}^4J_{PH}$ = 10 Hz) arising from cis, inequivalent PMe_3 ligands[12a] and a doublet of doublets at δ 0.42 ($^3J_{PH}$ = 10, 5 Hz) due to an Ir–Me group. The magnitudes of these couplings suggest that the methyl group is trans to one PMe_3 ligand and cis to the other.

The variation with time of the $^{31}P\{^1H\}$ NMR spectrum of the isopropyl complex **5b** in C_6H_6–CH_3OH (4:1 v/v) is reproduced in Figure 3. In addition to the singlet resonances of **5b** and **5a**, there appear two doublets at δ – 37.4 and −68.1 ($^2J_{PP}$ = 10 Hz) due to the cis, inequivalent PMe_3 ligands of the intermediate. When rearrangement is complete, only the resonances due to **5a** are present in the ^1H and $^{31}P\{^1H\}$ NMR spectra, those due to **5b** and the intermediate being absent. Unfortunately, neither the dispersion or the resolution of the ^1H NMR spectra are good enough to assign unambiguously the remaining peaks of the intermediate, so it is uncertain whether the compound contains a *n*-propyl or an isopropyl group. The compound is unlikely to be an alkene hydride such as **14** since no hydride resonance was observed in the region δ −9 to −12 typical of neutral and cationic hydridoalkylformyliridium(III) complexes.[13] The fact that δ(IrMe) for the intermediate is 0.42 rather than 0.60 suggests that the compound contains a *n*-propyl rather than an isopropyl group (see above), with a structure such as **15** (X = Br, I; R′ = Me). However, we cannot be sure that this correlation retains its validity for iridium(III) complexes containing cis PMe_3 ligands.

Dissolution of the (trimethylsilyl)methyl isopropyl complex **12b** in benzene–methanol at room temperature gives, on standing, a mixture of propene, tetramethylsilane, and $IrI(CO)(PMe_3)_2$, identified by their ^1H NMR spectra, in addition to the expected *n*-propyl complex **12a** (eq 3).



In C_6D_6–CD_3OD (10:1 v/v) reaction is complete within 10 h. The $^{31}P\{^1H\}$ NMR spectrum of the solution then shows only two singlets due to **12a** (62%) and $IrI(CO)(PMe_3)_2$

---

(13) Thorn, D. L. *J. Am. Chem. Soc.* **1980**, *102*, 7109.

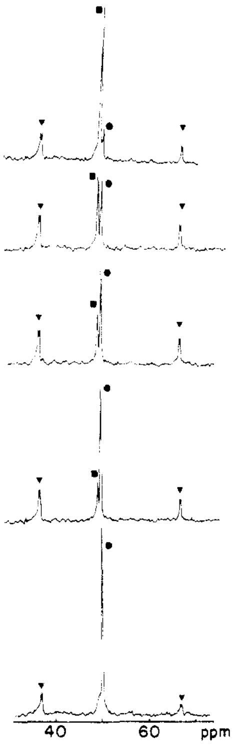
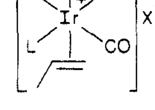
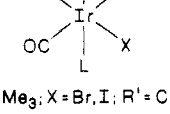


Figure 3. $^{31}P\{^1H\}$ NMR spectra of $IrIMe\{CH(CH_3)_2\}(CO)(PMe_3)_2$ (**5b**) in C_6H_6–CH_3OH (4:1 v/v) at 32 °C, showing formation of an intermediate containing cis PMe_3 ligands during isomerization to $IrIMe(CH_2CH_2CH_3)(CO)(PMe_3)_2$ (**5a**): ■, **5a**; ●, **5b**; ▼, intermediate.

(38%). Monitoring of the reaction by ^1H NMR spectroscopy provided evidence for an intermediate similar to that found in the methyliridium(III) system. The ^1H NMR spectrum of the intermediate shows a pair of P–Me doublets at δ 1.32 ($^2J_{PH} + {^4J_{PH}} = 8$ Hz) and 1.10 ($^2J_{PH} + {^4J_{PH}} = 10$ Hz) together with a singlet at δ 0.44 due to $IrCH_2SiMe_3$, but there is no hydride resonance. Unfortunately the other peaks of the intermediate could not be extracted from the many overlapping resonances. Since the *n*-propyl complex **12a** shows no tendency either to form the intermediate or to decompose to propene, $(CH_3)_4Si$, and $IrI(CO)(PMe_3)_2$ when it is dissolved in benzene–methanol (4:1 v/v) at 25 °C, it seems likely that the intermediate also contains a *n*-propyl group and has a structure such as **15** (R′ = CH_2SiMe_3); obviously other arrangements with cis phosphines are also possible.



14: L = PMe₃; X = Br, I

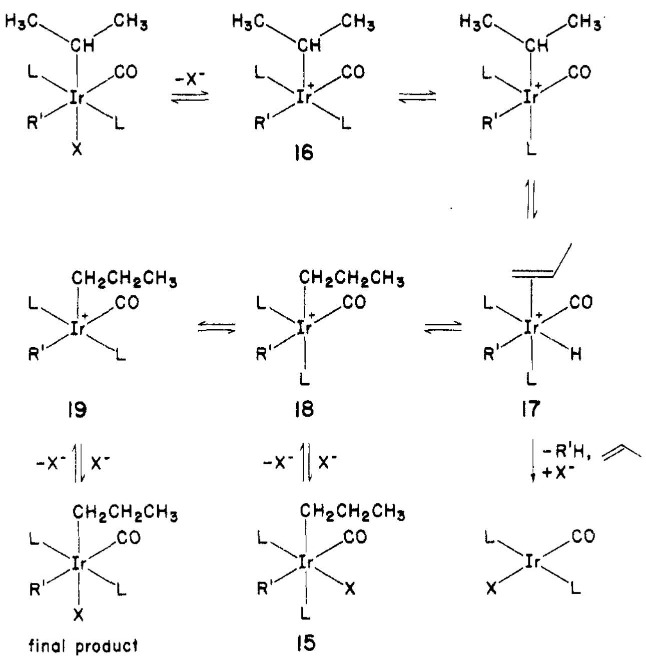


15: L = PMe₃; X = Br, I; R′ = CH₃, CH₂SiMe₃

The (trimethylsilyl)methyl *sec*-butyl complex **12d** also rearranges in benzene–methanol at room temperature to the *n*-butyl complex **12c**, together with a mixture of butene isomers, $(CH_3)_4Si$, and $IrI(CO)(PMe_3)_2$; the isomeric composition of the butenes could not be determined from the ^1H NMR spectrum and has not been investigated further. After 24 h the ratio of **12c** to $IrI(CO)(PMe_3)_2$ was about 4:1. An intermediate containing cis PMe_3 ligands can also be observed during this isomerization; its P–Me and Ir–Me ^1H NMR parameters are very similar to those of the corresponding propyl compound.

The phenyl *sec*-alkyl complexes **13b** and **13d** rearrange to the phenyl *n*-alkyl isomers **13a** and **13c**, respectively, in benzene–methanol at 25 °C. Qualitatively, the process is slower than that of the analogous CH_3 and CH_2SiMe_3 systems, e.g., the time required for complete conversion of **13b** into **13a** in C_6D_6–CD_3OD (5:1 v/v) is 24 h. In this case we were unable to observe any intermediate in the course of isomerization. This is in contrast to the CH_3 and CH_2SiMe_3 systems but like the chloro iodo monoalkyl complexes $IrClIR(CO)(PMe_3)_2$ discussed in the previous paper.[1] Kinetic data on alkyl rearrangement in the bis(alkyl) series have not yet been obtained, but, qualitatively, for a given alkyl group R in the complexes $IrIXR(CO)(PMe_3)_2$, the rate seems to vary with X in the order X = $Me_3SiCH_2 > CH_3 \approx Cl > I > C_6H_5$.

Scheme I



X = Br; L = PMe₃; R′ = CH₃

X = I; L = PMe₃; R′ = CH₃, CH₂SiMe₃, C₆H₅

Discussion

The *sec*- to *n*-alkyl group rearrangements of the bis(alkyl)iridium(III) complexes $IrXRR'(CO)(PMe_3)_2$ (X = Br, I) in solution resemble those of the monoalkyls $IrIClR(CO)L_2$ (L = PMe_3, PMe_2Ph)[1] and probably proceed by a similar mechanism in which the protic solvent methanol promotes dissociation of halide ion trans to the *sec*-alkyl group. The presence of the vacant coordination site in the resulting five-coordinate iridium(III) cation **16** initiates a series of reversible β-hydride migrations leading to the thermodynamically more stable *n*-alkyl complex, as outlined in Scheme I. In Scheme I, we assume that the observed intermediate having cis PMe_3 ligands is an essential element of the rearrangement process and not just part of a concurrent reaction. We assume also that it contains a *n*-alkyl group rather than a *sec*-alkyl group.

β-Hydride migration giving a cis hydrido olefin complex such as **17** presumably can occur only if the vacant site is cis to the isopropyl group, so **16** must rearrange. Perhaps at this stage the PMe_3 ligands adopt a cis arrangement, although movement of CO or R′ obviously would achieve the same end. Either the hydride can return to the coordinated alkene to give the rearranged alkyl cation **18** or it can undergo reductive elimination with the other alkyl or aryl group (R′ = CH_3, CH_2SiMe_3, or C_6H_5) to give alkane or arene (R′H), alkene, and $IrI(CO)(PMe_3)_2$. Direct return of halide ion to **18** gives the observed intermediate **15**

Table III. Analyses, Melting Points, and Molecular Weights of Bis(alkyl)iridium(III) Complexes $IrXRR'(CO)(PMe_3)_2$

		C		H		P	
alkyl group (R)	mp, °C	calcd	found	calcd	found	calcd	found
		$X = Br; R' = CH_3$					
$CH_2CH_2CH_3$ (**4a**)	90–95	25.9	26.2	5.5	5.6	12.1	12.3[a]
$CH(CH_3)_2$ (**4b**)	102–103	25.9	25.9	5.5	5.6		
$CH_2CH_2CH_2CH_3$ (**4c**)	65–66	27.5	27.2	5.8	5.6	11.8	12.4
$CH(CH_3)CH_2CH_3$ (**4d**)	85–86	27.5	27.4_5	5.8	5.8	11.8	12.0[b]
$CH_2[CH_2]_3CH_3$ (**4e**)	101–103	29.0	29.3	6.0	6.0_5	11.5	11.7_5
$CH(CH_3)CH_2CH_2CH_3$ (**4f**)	nm	29.0	29.1	6.0	6.0	11.5	11.7
		$X = I; R' = CH_3$					
$CH_2CH_2CH_3$ (**5a**)	115–120	23.7	23.9	5.1	5.0	11.1	11.4
$CH(CH_3)_2$ (**5b**)	121–122	23.7	23.9	5.1	5.2_5	11.1	11.3[c]
$CH_2CH_2CH_2CH_3$ (**5c**)	nm	25.2	25.2	5.3	5.3	10.8	10.9[d]
$CH(CH_3)CH_2CH_3$ (**5d**)	85–86	25.2	25.1	5.3	5.3_5	10.8	11.0
		$X = I; R' = CH_2SiMe_3$					
$CH_2CH_2CH_3$ (**12a**)	120–126	26.7	27.3	5.8	5.9	9.8	10.1[e]
$CH(CH_3)_2$ (**12b**)	118–120	26.7	26.4	5.8	5.9		
$CH_2CH_2CH_2CH_3$ (**12c**)	144–146	28.0	28.7	5.9_5	6.0	9.6	9.8[f]
$CH(CH_3)CH_2CH_3$ (**12d**)	62–63	28.0	27.8_5	5.9_5	5.9	9.6	9.8_5
		$X = I; R' = C_6H_5$					
$CH_2CH_2CH_3$ (**13a**)	nm	31.0	31.5	4.9	5.0	10.0	10.3
$CH_2CH_2CH_2CH_3$ (**13c**)	nm	32.3	32.3_5	5.1	5.1	9.8	9.4

[a] Mol wt: calcd, 510; found (CH_2Cl_2), 530. [b] Mol wt: calcd, 524; found (CH_2Cl_2), 503. [c] Mol wt: calcd, 557; found (CH_2Cl_2), 568. [d] Mol wt: calcd, 571; found (CH_2Cl_2), 556. [e] I: calcd, 20.2; found, 19.7_5. Mol wt: calcd, 630; found (CH_2Cl_2), 627. [f] I: calcd, 19.7; found, 19.6.

containing cis PMe_3 ligands, but this process is reversible and allows **18** to isomerize to **19**, containing trans PMe_3 ligands; attack of halide ion on **19** then gives the final, thermodynamically stable product. A related cis to trans rearrangement of tertiary phosphine ligands has been reported for $IrRCl_2(CO)(PMePh_2)_2$.[14] Reductive elimination is not observed at all when $R' = CH_3$ or C_6H_5, reflecting either a large kinetic barrier to this process or the thermodynamic stability of octahedral iridium(III) complexes relative to iridium(I) complexes. The bulk of Me_3SiCH_2 probably causes congestion in the coordination sphere of the *sec*-alkyl complexes containing this ligand, thus accounting for the competing reductive elimination of $(CH_3)_4Si$ observed with **5b** and **5d**, but even in these cases alkyl rearrangement to **5a** and **5c**, respectively, predominates.

The formation of bis(organo)iridium(III) complexes by oxidative addition of alkyl halides to organoiridium(I) species generated from $IrCl(CO)(PMe_3)_2$ and an organolithium reagent closely parallels chemistry based on rhodium(I) complexes that has been used to form carbon–carbon bonds. The substituted vinylrhodium(I) complex $Rh\{(E)\text{-}C(CO_2Me){=}CH(CO_2Me)\}(CO)(PPh_3)_2$ reacts with methyl or ethyl iodide to give isolable alkylvinylrhodium(III) complexes which, on rapid heating, reductively eliminate an *E*-trisubstituted olefin; i.e., the stereochemistry about the C═C bond is retained; slow heating causes formation of some of the (*Z*)-olefin.[15] Addition of acyl halides RCOCl to $RhR'(CO)(PPh_3)_2$ generated in situ from $RhCl(CO)(PPh_3)_2$ and R′Li provides a useful synthesis of ketones RCOR′, the assumed acylrhodium(III) intermediate being neither isolated nor detected.[16] Aryl iodides ArI react with $Rh(CH_3)(PPh_3)_3$ to give substituted toluenes $ArCH_3$ and $RhI(CO)(PPh_3)_2$, presumably via an intermediate methylphenylrhodium(III) complex.[17]

The high reactivity of the organoiridium(I) complexes $IrR'(CO)(PMe_3)_2$ is evidenced by their ability to oxidatively add *sec*-alkyl iodides and even, in the case of R′ = Me, *sec*-alkyl bromides; the adducts are formed cleanly provide the reagents are carefully purified. This sensitivity to purity may indicate that the reaction can follow a variety of radical pathways depending on conditions, somewhat like the addition of alkyl halides to d^{10} metal complexes such as PtL_3 (L = PEt_3, PPh_3).[18] Despite their reactivity, however, the usefulness of the iridium(I) complexes in organic synthesis is likely to be limited by the reluctance of the iridium(III) adducts to reductively eliminate their alkyl or aryl groups and by the facile *sec*- to *n*-alkyl group isomerization promoted by protic solvents that we have demonstrated.

Experimental Section

Preparative and spectroscopic techniques were generally as described in part 1.[1] IR spectra in the range 400–100 cm^{-1} were recorded as polythene disks on a Hitachi FIS-3 grating spectrometer. For the preparation of the organoiridium(I) complexes, all glassware was flame-dried in vacuo, Celite was dried at 250 °C for 24 h before use, and NMR solvents were freeze-thawed in vacuo four times and stored in a Vacuum Atmospheres Drilab. Methyllithium in ether and phenyllithium in benzene–ether (70:30) were obtained commercially; [(trimethylsilyl)methyl]lithium,[19] $IrCl(CO)(PMe_3)_2$,[20] $IrCl(CO)(PMe_2Ph)_2$[21] and $IrCl(CO)(PPh_3)_2$[22] were prepared by literature procedures. Alkyl halides were distilled under nitrogen and, immediately before each reaction, were then vacuum distilled from P_4O_{10} at room temperature.

Analytical, melting point, molecular weight data for the bis(organo)iridium(III) complexes are in Table III.

Preparations. Carbonylbis(trimethylphosphine)methyliridium(I), $Ir(CH_3)(CO)(PMe_3)_2$ (1). Methyllithium (1.23 mmol) was added dropwise to a stirred solution of $IrCl(CO)(PMe_3)_2$ (0.50 g, 1.23 mmol) in toluene (15 mL) at −78 °C. The solution was allowed to warm to room temperature over a

---

[14] Bennett, M. A.; Jeffery, J. C. *Inorg. Chem.* **1980**, *19*, 3763.

[15] Schwartz, J.; Hart, D. W.; Holden, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 9269.

[16] Hegedus, L. S.; Lo, S. M.; Bloss, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 3040.

[17] Semmelhack, M. F.; Ryono, L. *Tetrahedron Lett.* **1973**, 2967.

[18] Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; Chapter 7, pp 162–166 and references cited therein.

[19] Connolly, J. W.; Urry, G. *Inorg. Chem.* **1963**, *2*, 645.

[20] Labinger, J. A.; Osborn, J. A. *Inorg. Synth.* **1978**, *18*, 62.

[21] Shaw, B. L.; Singleton, E. *J. Chem. Soc. A* **1967**, 1683.

[22] Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

2-h period and stirred for a further 2 h. Solvent was removed from the orange solution in vacuo, and the yellow residue was extracted with hexane (2 × 20 mL). The solution was filtered through Celite and stored at −78 °C for 48 h. The resulting yellow crystals were dried in vacuo, giving 0.22 g (47%) of 1: mp 122–124 °C; IR (Nujol) 1935 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 1.36 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), 0.50 (t, $^3J_{PH}$ = 10 Hz, $IrCH_3$); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −21.8 (s). Anal. Calcd for $C_8H_{21}IrOP_2$: C, 24.8; H, 5.5; P, 16.0. Found: C, 24.8; H, 5.7; P, 16.0.

Carbonylbis(trimethylphosphine)[(trimethylsilyl)methyl]iridium(I), $Ir(CH_2SiMe_3)(CO)(PMe_3)_2$ (2). This was prepared similarly to 1 from ethereal [(trimethylsilyl)methyl]lithium (1.70 mmol) and $IrCl(CO)(PMe_3)_2$ (0.69 g, 1.69 mmol) in toluene (15 mL) at −78 °C. The yield of yellow, crystalline 2 was 0.47 g (58%): mp 85–86 °C; IR (Nujol) 1935 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 1.48 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), 0.44 (t, $^3J_{PH}$ = 14 Hz, $IrCH_2SiMe_3$), 0.40 (s, $IrCH_2SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −25.1 (s). Anal. Calcd for $C_{11}H_{29}IrOP_2Si$: C, 28.7; H, 6.4; P, 13.5. Found: C, 28.8; H, 6.8; P, 13.2.

Carbonylbis(trimethylphosphine)phenyliridium(I), $Ir(C_6H_5)(CO)(PMe_3)_2$ (3). This was prepared similarly to 1 from phenyllithium (1.50 mmol) and $IrCl(CO)(PMe_3)_2$ (0.60 g, 1.47 mmol) in toluene (15 mL) at −78 °C. After being allowed to come to room temperature (2 h), the solution was stirred for a further 4 h and evaporated to dryness in vacuo. The residue was extracted with hexane (3 × 20 mL) and filtered through Celite. The yellow solution was cooled to −78 °C for 24 h, and the resulting yellow crystals were dried in vacuo to give 0.57 g (86%) of 3: mp 115–118 °C; IR (Nujol) 1940 cm^{-1} (CO); ^1H NMR (CD_2Cl_2) 7.5–7.0 (m, C_6H_5), 1.12 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −22.3 (s). Anal. Calcd for $C_{13}H_{23}IrOP_2$: C, 34.7; H, 5.2; P, 13.8. Found: C, 35.6; H, 5.5; P, 13.9.

Carbonylbis(triphenylphosphine)[(trimethylsilyl)methyl]iridium(I), $Ir(CH_2SiMe_3)(CO)(PPh_3)_2$. A solution of $IrCl(CO)(PPh_3)_2$ (0.50 g, 0.64 mmol) in THF (20 mL) at 25 °C was treated dropwise with ethereal Me_3SiCH_2Li (1.0 mmol), and the orange solution was stirred for 18 h. The solution was concentrated to ca. 5 mL in vacuo and applied to a column of neutral alumina (Grade 1) (ca. 2 cm × 30 cm) maintained at −30 °C. Elution with ether (ca. 100 mL) and evaporation to dryness in vacuo gave a yellow solid (0.2 g) which still retained ca. 0.5–1.0 mmol of ether. The solid was identified as $Ir(CH_2SiMe_3)(CO)(PPh_3)_2$ by its NMR and IR spectra: IR (Nujol) 1914 cm^{-1} (CO); ^1H NMR (C_6D_6) δ 0.83 (t, $^3J_{PH}$ = 12 Hz, $IrCH_2SiMe_3$), 0.03 (s, $IrCH_2SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 26.9 (s).

Carbonylbis(dimethylphenylphosphine)[(trimethylsilyl)methyl]iridium(I), $Ir(CH_2SiMe_3)(CO)(PMe_2Ph)_2$. A solution of $IrCl(CO)(PMe_2Ph)_2$ (0.20 g, 0.38 mmol) in toluene (10 mL) at −78 °C was treated with ethereal Me_3SiCH_2Li (0.4 mmol). Workup as for 1 gave 0.1 g (45%) of yellow, crystalline $Ir(CH_2SiMe_3)(CO)(PMe_2Ph)_2$, identified by NMR spectroscopy: ^1H NMR (C_6D_6) δ 1.90 (t, $^2J_{PH} + {}^4J_{PH}$ = 6 Hz, PCH_3), 0.57 (t, $^3J_{PH}$ = 13 Hz, $IrCH_2SiMe_3$), 0.21 (s, $IrCH_2SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ −10.9 (s).

Alkylbis(trimethylphosphine)carbonylhalogenomethyliridium(III), $IrXMeR(CO)(PMe_3)_2$ (4a–f; 5a–d). A solution of $IrMe(CO)(PMe_3)_2$ (1) (0.08 g, 0.21 mmol) in benzene (5 mL) was treated with the appropriate alkyl halide (0.1 mL) at room temperature. The yellow solution turned paler or colorless over 1–10 min. The solution was stirred for 30 min (60 min in the case of branched alkyl bromides) to ensure complete reaction. Solvent was removed under vacuum, and the residue was extracted with hexane (2 × 5 mL). The extracts were filtered through Celite, and the colorless solution was set aside at −78 °C for 48 h to give colorless crystals of the required complexes which were dried in vacuo. Yields were generally 60–70%. Although the complexes appeared to be air-stable as solids and in solution, they were stored under nitrogen at −10 °C and samples for NMR studies were prepared in the drybox.

Alkylbis(trimethylphosphine)carbonyliodo[(trimethylsilyl)methyl]iridium(III), $IrI(CH_2SiMe_3)R(CO)(PMe_3)_2$ (12a–d). These were prepared similarly to 5a–d from 2 (0.08 g, 0.17 mmol) in benzene (5 mL) and the appropriate alkyl iodide at room temperature. The colorless crystals were obtained in 70–80% yield. The *n*-alkyls were air-stable as solids and in solution, but the *sec*-alkyls were stored under nitrogen at −10 °C owing to their thermal instability. Solutions for NMR studies were prepared in the drybox.

Alkylbis(trimethylphosphine)carbonyliodophenyliridium(III), $IrIPhR(CO)(PMe_3)_2$ (13a–d). These were prepared similarly to 5a–d from 3 (0.08 g, 0.18 mmol) in benzene (5 mL) and the appropriate alkyl iodide at room temperature. The yellow solution became colorless within 2–10 min. After the usual workup, yields of the colorless adducts were 70–80%.

Isomerization of *sec*-Alkyl Complexes. (1) A solution of 4b in C_6D_6 (0.5 mL) and CD_3OD (0.1 mL) was prepared in a 5-mm NMR tube, and successive ^1H NMR spectra were recorded at 29 °C. Up to 0.5 h only resonances due to the isopropyl complex 4b were present, but after 24 h these had disappeared and had been replaced by resonances due to the *n*-propyl complex 4a. In the period 1–10 h after dissolution, signals due to an intermediate were observed, as described in the text and illustrated in Figures 1 and 2.

The isomerization of a solution of 4b in benzene (0.5 mL) and methanol (1 mL) contained in a 5-mm NMR tube was also monitored by $^{31}P\{^1H\}$ NMR spectroscopy at 35 °C. The singlet resonance of 4b at δ −46.5 was replaced by that due to 4a at δ −45.6, and a pair of doublets at δ −36.4 and −61.4 ($^2J_{PP}$ = 10 Hz) due to the intermediate was observed.

The rearrangement of 5b to 5a was studied similarly. The NMR parameters of the intermediate are as follows: ^1H, δ 1.34 (d, $^2J_{PH} + {}^4J_{PH}$ = 9 Hz, PCH_3), 0.98 (d, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz, PCH_3), 0.57 (m, $IrCH_3$); ^{31}P, δ −37.4 (d), −68.1 (d) ($^2J_{PP}$ = 10 Hz).

(2) The ^1H NMR spectrum of a solution of 12b in C_6D_6 (0.5 mL) and CD_3OD (0.05 mL) was recorded at 29 °C. Up to 0.3 h only resonances due to 12b were present, but after 24 h signals due to four species were observed: the *n*-propyl isomer 12a; $IrI(CO)(PMe_3)_2$, δ 1.47 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3); propene, δ 5.90–5.50 (m, $CH_2{=}CHCH_3$), 5.06–4.86 (m, $CH_2{=}CHCH_3$), 1.65–1.55 (m, $CH_2{=}CHCH_3$); tetramethylsilane, δ 0.0 (s). Between 0.5 and 7.0 h, resonances due to an intermediate were also observed at δ 1.32 (d, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3), 1.10 (d, $^2J_{PH} + {}^4J_{PH}$ = 10 Hz, PCH_3) and 0.44 (s, $IrCH_2SiMe_3$).

The $^{31}P\{^1H\}$ NMR spectrum after 24 h showed singlets at δ −52.1 and −24.8 in a ratio of 62:38 due to 12a and $IrI(CO)(PMe_3)_2$, respectively.

The rearrangement of the *sec*-butyl complex 12d proceeded similarly. Up to 0.3 h only resonances due to 12d were observed, but after 24 h signals due to four species were present: the *n*-butyl isomer 12c; $IrI(CO)(PMe_3)_2$, δ 1.47 (t, $^2J_{PH} + {}^4J_{PH}$ = 8 Hz, PCH_3); butene, δ 5.4 (m, olefinic protons); tetramethylsilane, δ 0.0 (s). The CH_3 protons of butene could not be located. The butene may be a mixture of isomers, but it was not possible to identify these conclusively from the ^1H NMR spectrum. *cis*- and *trans*-2-butene have olefinic resonances at δ 5.35, whereas 1-butene has olefinic resonances at δ 5.9–5.5 and 5.0–4.8.[23]

The $^{31}P\{^1H\}$ NMR spectrum after 24 h showed singlets at δ −52.4 and −25.0 in a ratio of 79:21 due to 12c and $IrI(CO)(PMe_3)_2$, respectively.

The rearrangements of 13b and 13d to 13a and 13c, respectively, were studied similarly, but in these cases no intermediate containing cis PMe_3 ligands could be detected.

Addition of Methyl Halides to $IrY(CO)(PMe_3)_2$. A solution of $IrBr(CO)(PMe_3)_2$ (0.08 g, 0.18 mmol) in benzene (5 mL) was treated with an excess of methyl iodide (ca. 0.15 mL). The initially yellow solution rapidly turned colorless. Evaporation of solvents and trituration with hexane gave $IrBrIMe(CO)(PMe_3)_2$ (9) as a white solid (0.08 g, 75%): IR (Nujol) 2020 cm^{-1} (CO); IR (polythene disk) 280 (PC_3 def), 192 cm^{-1} (IrBr).

Addition of methyl bromide to $IrBr(CO)(PMe_3)_2$ and to $IrCl(CO)(PMe_3)_2$ gave respectively $IrBr_2Me(CO)(PMe_3)_2$ (10) and $IrClBrMe(CO)(PMe_3)_2$ (11). 10: IR (Nujol) 2030 cm^{-1} (CO); IR (polythene disk) 280 (PC_3 def), 192, 168 cm^{-1} (IrBr). 11: IR (Nujol) 2025 (CO), 300 (IrCl), 280 cm^{-1} (PC_3 def), 168 cm^{-1} (IrBr).

Registry No. 1, 103190-94-9; 2, 103190-95-0; 3, 103190-96-1; 4a, 103190-97-2; 4b, 103190-98-3; 4c, 103190-99-4; 4d, 103191-00-0;

---

[23] *Selected NMR Spectral Data (100 MHz)*; American Petroleum Research Institute Project 44, Thermodynamics Research Center: Texas A&M University, College Station, TX, Serial Nos. 217c (1-butene), 218c (*cis*-2-butene), 219c (*trans*-2-butene).

4e, 103191-01-1; **4f**, 103191-02-2; **5a**, 103191-03-3; **5b**, 103191-04-4; **5c**, 103191-05-5; **5d**, 103191-06-6; **9**, 103191-16-8; **10**, 103191-17-9; **11**, 74511-68-5; **12a**, 103191-07-7; **12b**, 103191-08-8; **12c**, 103191-09-9; **12d**, 103191-10-2; **13a**, 103191-11-3; **13b**, 103191-14-6; **13c**, 103191-12-4; **13d**, 103191-15-7; $IrCl(CO)(PMe_3)_2$, 21209-86-9; $Ir(CH_2SiMe_3)(CO)(PPh_3)_2$, 82180-73-2; $IrCl(CO)(PPh_3)_2$, 15318-31-7; $Ir(CH_2SiMe_3)(CO)(PMe_2Ph)_2$, 103191-13-5; $IrCl(CO)(PMe_2Ph)_2$, 21209-82-5; $IrBr(CO)(PMe_3)_2$, 65016-02-6.

Binuclear Complexes of Nickel(0): Comparison of a Bridging Methyl Isocyanide and a Bridging (Methylamino)carbyne Ligand

Dru L. DeLaet, Phillip E. Fanwick,[†] and Clifford P. Kubiak*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received January 27, 1986

The reduction of the Ni^I species $[Ni_2(\mu\text{-}CNMe)(CNMe)_3(PPh_2CH_2PPh_2)_2][PF_6]_2$ (**1**) with sodium amalgam leads to the formation of the complex $Ni_2{}^0(\mu\text{-}CNMe)(CNMe)_2(PPh_2CH_2PPh_2)_2$ (**2**), the crystal and molecular structure of which has been determined. Complex **2** crystallizes in the monoclinic space group $C2/c$ with $a = 22.645$ (3) Å, $b = 12.662$ (2) Å, $c = 35.126$ (4) Å, $\beta = 98.017$ (9)°, $V = 9973.0$ (4) Å^3, and $Z = 8$. The structure was refined to convergence leading to R and R_w of 0.060 and 0.082, respectively, for 3682 observations in the range $6° \leq 2\theta \leq 110°$ with $I \geq 3.0\sigma(I)$ (Cu Kα radiation). The Ni–Ni separation is 2.572 (1) Å consistent with a Ni–Ni bond. The molecular structure of **2** displays unusual cis,cis bridging diphosphine ligands. The bridging CNMe ligand of the complex is very basic and can be easily protonated by weak acids to form $[Ni_2{}^0(\mu\text{-}CNMeH)(CNMe)_2(PPh_2CH_2PPh_2)_2]\cdot[PF_6]$ (**3**), the crystal and molecular structure of which also has been determined. Complex **3** crystallizes in the monoclinic space group Cc with $a = 23.124$ (3) Å, $b = 12.941$ (2) Å, $c = 20.792$ (3) Å, $\beta = 117.00$ (1)°, $V = 5544.0$ (3) Å^3, and $Z = 4$. The structure was refined to convergence leading to R and R_w of 0.057 and 0.073, respectively, for 3435 observations in the range $6° \leq 2\theta \leq 120°$ with $I \geq 3.0\sigma(I)$. In comparison to complex **2**, **3** possesses a shorter Ni–Ni separation of 2.500 (1) Å, shorter C–Ni bond distances for the bridging ligand, and longer Ni–C bond lengths for the terminal CNMe groups. These observations, along with spectroscopic data, are interpreted in terms of a greater contribution of an aminocarbyne valence bond description to the bonding of **3** compared to **2**.

Introduction

The use of two or more metals for the selective activation of molecular substrates remains an important objective for organometallic chemists.[1] We report the preparation and reactivity of new binuclear isocyanide complexes of Ni(0). These complexes possess unusual *cis,cis*-$(dppm)_2$ (dppm = bis(diphenylphosphino)methane) structures. They also possess bridging isocyanide ligands which have Lewis basicities exceeding that of ammonia and thus can be protonated or alkylated under very mild conditions to afford bridging (alkylamino)- or (dialkylamino)carbyne species. Together the new complexes reported also provide an interesting comparison between the structure and reactivity of a bridging methyl isocyanide and a bridging (methylamino)carbyne ligand in essentially identical dimetallic environments.

Experimental Section

Materials. All solvents were deoxygenated prior to use. Iodomethane (EM Science), hexane, and toluene (Fisher Scientific) were used without further purification. Tetrahydrofuran was freshly distilled from sodium/benzophenone. $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2$ was prepared as previously reported.[2]

Physical Measurements. Elemental analyses were performed by Dr. H. D. Lee of the Microanalytical Laboratory, Department of Chemistry, Purdue University, and also Galbraith Laboratories, Inc. Difficulty was encountered in obtaining satisfactory analyses for carbon in the nickel complexes reported here due to the formation of Ni_3C. Satisfactory results were obtained by Galbraith Laboratories using high-temperature combustion (>1500 °C) with a High Temperature Leco Inc. analyzer. UV–vis spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier transform infrared spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer. ^1H NMR was measured against internal Me_4Si and $^{31}P\{^1H\}$ NMR against external 85% H_3PO_4.

Synthesis of $Ni_2(CNMe)_3(dppm)_2$ (2). A slurry of $[Ni_2(CNMe)_4(dppm)_2][PF_6]_2$ (0.1 g) in 25 mL of toluene was stirred over an excess of Na/Hg. After 18 h, a bright red solution was obtained. This was filtered and reduced in volume to 5 mL. Precipitation of a bright red crystalline solid was accomplished by slow addition of an equal volume of hexane: total yield 0.058 g (77%); ^1H NMR (C_7D_8, –30 °C) δ 2.44 (s, 3 H), 2.55 (s, 6 H), 4.31 (m, 4 H), 7.2–8.1 (m, 40 H); $^{31}P\{^1H\}$ NMR (toluene-d_8, 25 °C) δ 18.21 (s); IR (toluene) ν(CN) 2075, 1717 cm^{-1}; UV–vis (λ_{max}, nm (ϵ)) 395 (15 000). Anal. Calcd for $C_{56}H_{53}N_3Ni_2P_4$: C, 66.64; H, 5.29; N, 4.16. Found: C, 66.60, H, 5.23, N, 4.09.

Synthesis of $[Ni_2(CNMeH)(CNMe)_2(dppm)_2]\cdot[PF_6]$ (3). To a solution of **2** (0.1 g) in 20 mL of THF was added 1 equiv of $[HOEt_2][PF_6]$ (16 μL). The red solution immediately became dark green. Precipitation was effected by addition of 10 mL of hexane. The crystalline solid was filtered, washed with hexane, and dried under vacuum: total yield 0.076 g (66%); IR (Nujol) ν(CN) 2135, 1525 cm^{-1}, ν(NH) 3338 cm^{-1}, ν(ND) 2480 cm^{-1} when $F_3C_2O_2D$ was used; $^{31}P\{^1H\}$ δ 19.75 (AA′BB′); ^1H NMR (25 °C) δ 2.48 (s, 3 H), 3.28 (s, 6 H), 3.70 (br s, 4 H), 6.8–7.6 (m, 40 H). Anal. Calcd for $C_{56}H_{54}N_3Ni_2P_5F_6$: C, 58.22; H, 4.71; N, 3.64. Found: C, 58.13; H, 4.69; N, 3.32.

Synthesis of $[Ni_2(CNMe_2)(CNMe)_2(dppm)_2]I$ (4). To a solution of **2** (0.1 g) in 20 mL of THF was added 1 equiv of CH_3I (6.3 μL). Precipitation of a dark green crystalline solid was initiated by addition of ~10 mL of hexane. The solid was washed with hexane and dried under vacuum: total yield 0.099 g (87%);

[†] Address correspondence pertaining to crystallographic studies to this author.

(1) See, for example; Schore, N. E.; Ilenda, C. S.; White, M. A.; Bryndza, H. E.; Matturro, M. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7451 and references therein.

(2) DeLaet, D. L.; Powell, D. R.; Kubiak, C. P. *Organometallics* **1985**, *4*, 954.

0276-7333/86/2305-1807$01.50/0 © 1986 American Chemical Society