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(Phosphinoalkyl)silyl Complexes. 11.[1] Structural Influence of the Chelate Dimethyl((diphenylphosphino)ethyl)silyl Group. Irregular 5-Coordinate Geometry at a d^6 Center. X-ray Crystal and Molecular Structures of Three Silyliridium(III) Complexes [Ir(chel)$_2$Cl, IrH(chel)(PPh$_3$)(CO)Cl, IrH(chel)(cod)Cl; chel = PPh$_2$CH$_2$CH$_2$SiMe$_2$−, cod = Cycloocta-1,5-diene]

Mary J. Auburn,[†] Rupert D. Holmes-Smith,[†] Stephen R. Stobart,*,[†]
Pradip K. Bakshi,[‡] and T. Stanley Cameron[‡]

*Departments of Chemistry, University of Victoria, British Columbia, Canada V8W 2Y2, and
Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3*

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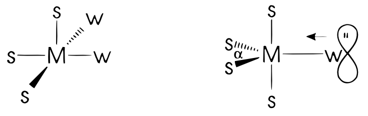
The bis((phosphinoalkyl)silyl)iridium(III) complex Ir(chel)$_2$Cl (**6**; chel = PPh$_2$CH$_2$CH$_2$SiMe$_2$−), which has been characterized by using single-crystal X-ray crystallography, displays a distorted trigonal bipyramidal (dist-TBP) geometry in which the equatorial Si−Ir−Si angle is very narrow, at 86.3(3)°, with the Si−Ir−Cl angles correspondingly wide, 134.8(2) and 138.9(2)°. All bonds to Ir in the equatorial plane are short compared with corresponding distances in two directly related structures, those of the six-coordinate ((phosphinoalkyl)silyl)iridium(III) compounds IrH(chel)(PPh$_3$)(CO)Cl **(7)** and IrH(chel)(cod)Cl (**8**; cod = cycloocta-1,5-diene): thus Ir−Si = 2.302(7), 2.315(8) Å in **6** *vs* 2.41(1), 2.364(5) Å in **7** and **8**, respectively, while Ir−Cl = 2.381(6) Å in **6** *vs* 2.503(8), 2.495(5) Å in **7** and **8**, respectively. The distortions in the dist-TBP geometry of **6** are discussed in relation to structures of a small family of related 16e complexes and in terms of ligand trans influences.

Pentacoordinate transition-metal centers offer a clearly recognizable link between unsaturated square-planar geometry and the corresponding saturated octahedral state, and accordingly, the behavior of such systems is viewed as possessing special significance in relation to reactivity. Distortion of regular trigonal bipyramidal (TBP) ML$_5$ coordination has been observed to lead almost invariably to a square-pyramidal (SQP) arrangement, **A**: in particular, it is this structure that is adopted by virtually all d^6 ML$_5$ complexes, where it is characterized by an open site trans to the most strongly trans-influencing atom or group in the ligand set. Recently, however, a well-defined alternate geometry has been recognized by Eisenstein, Pelissier *et al.*:[2] it occurs when four (rather than three, SQP) of the five ligands L exert a strong trans influence (2 axial, *ax*, with 2 equatorial, *eq*). In such circumstances, a distorted trigonal bipyramidal (dist-TBP) structure **B** is observed, in which the angle α between bonds to the strong (*i.e. strongly* trans-influencing) *eq* ligands is characteristically narrow (<90°), while the bond distance to the remaining, weak (*i.e. weakly* trans-influencing) *eq* ligand may be shorter than normal. These unique features have been rationalized in theoretical terms,[2] elaborating on earlier predictions of Thorn and Hoffmann:[3] in ab initio calculations that explore the relationship of **A** with **B**, the X-ray crystal structures of the iridium(III) complexes Ir[N(SiMe$_2$CH$_2$PPh$_2$)$_2$](R)(R′) (**1**, R = Me, R′ = CH$_2$CMe$_3$ or R = R′ = CH$_2$Ph: Fryzuk *et al.*,[4] 1986) (see Chart 1) and IrH(Ph)(Cl)(PCy$_3$)$_2$ (**2**: Werner *et al.*,[5] also 1986) were used as preliminary experimental models. The calculations have since been developed further around the geometry of an analogue[6] IrH$_2$(Cl)(P^{t}Bu$_2$Ph)$_2$ **(3)** of the iridium(III) dihydride IrH$_2$(Cl)(P^{i}Pr$_3$)$_2$, a compound that was first isolated[7] in 1985 also by Werner *et al.* In the structure of **3**, which has been determined[6] by Caulton, Eisenstein *et al.* using neutron diffraction, the hydride ligands were found in positions that subtend a



A: SQP B: "dist-TBP"

(s = strongly, w = weakly
trans influencing ligand L)

[†] University of Victoria.

[‡] Dalhousie University.

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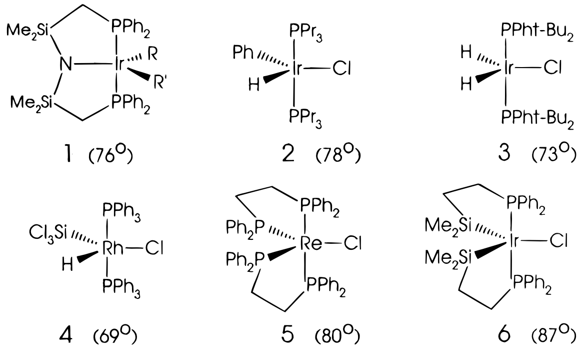
Chart 1



narrow angle (73°) at Ir, resembling those between R, R′ (76°) and between H and Ph (78°) in **1** and **2**, respectively: *i.e.* structures **1**−**3** all belong to type **B**.

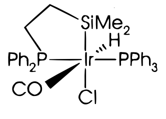
Refinement of the theoretical description of the dist-TBP geometry **(B)** as it relates to the observed structure for **3** has focused as a pivotal issue on the π-donor capacity of the single weak *eq* ligand: the contracted M−L$_{eq}$ distance to the latter is interpreted[6] *ipso facto* in terms of back-donation of nonbonding electron density from L$_{eq}$ onto the electron-deficient (16e) metal center M. While this is a credible proposition, new crystallographic data that are compared below suggest its importance may have been overestimated. At least three related dist-TBP structures predate those of compounds **1**−**3**: a similarly acute L$_{eq}$ML$_{eq}$ angle is evident in the Rh(III) complexes RhH(PPh$_3$)$_2$(SiCl$_3$)(Cl) (**4**: Ibers *et al.*,[8] 1970) and in the Re(I) complex Re(diphos)$_2$Cl (**5**, diphos = Ph$_2$PCH$_2$CH$_2$PPh$_2$: Pombeiro, Richards *et al.*,[9] 1983) as well as in a further Ir(III) analogue Ir(chel)$_2$Cl (**6**, chel = Ph$_2$PCH$_2$CH$_2$SiMe$_2$−), which was reported[10] from this laboratory in 1985 although only a summary of the gross geometry was supplied. The relationship between geometries **A** and **B** is also explicitly defined by the molecular structures of the rhodium(III) complexes RhHCl$_2$(P^{i}Pr$_3$)$_2$ and RhH$_2$Cl(P^{i}Pr$_3$)$_2$, which were the more recent subjects of an elegant crystallographic study by Harlow *et al.*[11]

The structure of compound **6** is compared below with those of two closely related *octahedral* systems (one of which is itself of considerable interest as a rare example of a structurally characterized *cis*-hydrido−olefin complex); this shows that in terms of criteria applied elsewhere[6] to **3**, in **6** *all three* of the M−L$_{eq}$ bonds are shorter than expected. The same effect has been distinguished recently by Morris *et al.*[12] in the *eq* plane around the 16e d^6 metal center in the Ru(diphos)$_2$Cl$^+$ cation, *i.e.* which is isoelectronic with **6** (and **1**−**3**), as well as by Kubas *et al.*[12b] in the Tc analogue of complex **5**.

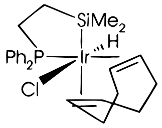
Results

The chemistry of chelate (phosphinoalkyl)silyl ("PSi") complexes of the platinum-group metals ("PGMs") has been under investigation in this laboratory since the early 1980s. An extensive family of such molecules[1,10,13] now exists in which the uniquely strong trans-labilizing capacity of the silyl group[10,14] is held in contact with a reactive metal center by simultaneous coordination through phosphorus donor sites incorporated into a polyfunctional framework. The architecture of this type of hybrid complexation (*i.e.* by Si and P) is that in which one phosphorus atom in the familiar, neutral, usually bidentate ligand diphos is replaced by silicon,[1] so forming the isoelectronic silyl PPh$_2$CH$_2$CH$_2$SiMe$_2$−(chel). Attachment of the PSi ligand is accomplished by oxidative addition of the corresponding silane (chelH) at a low-valent PGM center.

To date the crystal structure of only one chel complex, *viz.* Os(chel)$_2$(CO)$_2$, has been discussed in full,[15] although outline descriptions of molecular geometry have been provided[1,10,16,17] for Pt(chel)$_2$, Ir(chel)$_2$Cl, and Ir(chel)(CO)$_2$(PPh$_3$). Complete details of the X-ray crystal and molecular structures of three chel complexes of iridium(III) are presented here: the three molecules are of particular interest, each for different reasons. Thus IrH(chel)(CO)(PPh$_3$)Cl **(7)**, which is formed[13] as a single geometric isomer (racemate), offers a prototypal structurally characterized example of an octahedral center from which bonds extend to six different atoms, *i.e.* a chiral OC-6-iridium center.[13] The second complex, IrH(chel)(cod)Cl (**8**, cod = cycloocta-1,5-diene), is also asymmetric at the Ir center; more significantly, however, it offers a still very rare example[10] of a stable *cis*-hydrido−olefin geometry, in a product that shows no tendency to undergo spontaneous intramolecular alkyl formation *via* migratory insertion. In the presence of stronger donors, the chelating diolefin in **8** can be induced to eliminate,[10] so that addition of excess chelH affords a further chel compound, Ir(chel)$_2$Cl **(6)**.



7



8

A. X-ray Crystal and Molecular Structure of Compound 7. A *rac*-OC-6-iridium(III) Center. We have discussed elsewhere the existence of enantiomeric **7** as a single geometrical isomer and have named the complex referring to rules for priority sequencing in such systems.[13] There are eight molecules in the unit cell of **7** (space group $P2_1/n$: Table 1); *i.e.* the asymmetric unit contains two molecules, but these in fact differ only very slightly from one another (see below). Molecule **a** (centered on Ir(1)) is depicted as an ORTEP drawing in Figure 1, the caption to which sets out important bond distances and angles; a PLUTO plot showing both molecules is included as a part of the Supporting Information, together with full tables of bond distances

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Table 1. Crystal Data[a] for Compounds 6−8

	6	7	8
chem formula	$C_{32}H_{40}Si_2P_2ClIr$	$C_{35}H_{35}OSiP_2ClIr$	$C_{24}H_{32}SiPClIr$
fw	770.4	789.3	607.22
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Z	4	8	4
a, Å	12.321(2)	11.521(2)	9.476(3)
b, Å	15.358(3)	20.053(6)	17.116(8)
c, Å	17.212(2)	29.898(4)	15.067(5)
B, deg	96.30(1)	96.03(3)	103.83(3)
V, Å^3	3237(2)	6869(4)	2374(3)
$F(000)$	1536	3128	1196
Q_{calcd}, g cm^{-3}	1.581	1.526	1.699
μ(Mo Kα), cm^{-1}	43.82	41.02	58.42
rflns collcd	4636	6584	3360
unique rflns	4472	6428	3104
rflns obsd ($I > 3\sigma(I)$)	1793	2469	1547
no. of variables	343	620	271
R^b	0.0488	0.0508	0.0378
$R_w{}^b$	0.0498	0.0520	0.0372

[a] All data collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.070\ 926$ Å) at 291 K using a CAD4 diffractometer. Scan type: $\omega-2\theta$. Scan range θ: (1.35 + 0.35 scan θ)°; $2\theta_{max}$, 46.0° throughout. [b] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = \Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

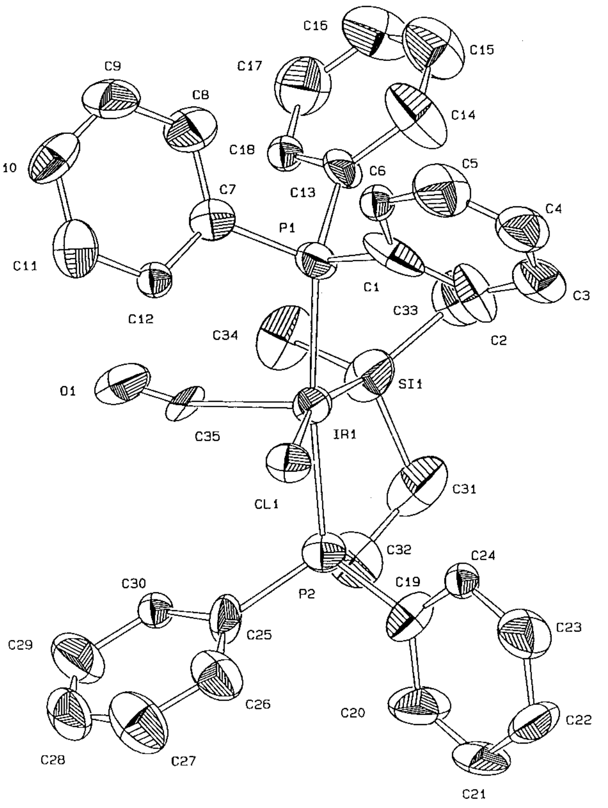

Figure 1. ORTEP plot of IrH(chel)(CO)(PPh_3)Cl **(7)**, molecule **a** (see text). Selected distances (Å) and angles (deg): Ir(1)−Cl(1), 2.503(8); Ir(1)−P(1), 2.361(9); Ir(1)−P(2), 2.315(9); Ir(1)−Si(1), 2.411(12); Ir(1)−C(35), 2.00(2); 0(1)−C(35), 1.02(4); Cl(1)−Ir(1)−P(1), 88.0(3); Cl(1)−Ir(1)−P(2), 86.3(3); Cl(1)−Ir(1)−Si(1), 164.3(3); Cl(1)−Ir(1)−C(35), 98.1(7); P(1)−Ir(1)−P(2), 171.2(3); P(1)−Ir(1)−Si(1), 100.0(4); P(1)−Ir(1)−C(35), 97.2(7); P(2)−Ir(1)−Si(1), 84.1(4); P(2)−Ir(1)−C(35), 90.3(7); Si(1)−Ir(1)−C(35), 94.4(8); Ir(1)−C(35)−0(1), 163(3).

and angles, fractional atomic coordinates, and thermal parameters. Bond lengths are identical to within error for molecules **a** and **b** (around Ir(1) and Ir(2), respectively) except for Ir(1)−C(35) = 2.00(2) *vs* Ir(2)−C(70) = 1.84(3) Å, the latter distance arising from slight disorder in the carbonyl group of molecule **b** (see Supporting Information). The hydride ligand (*i.e.* H bonded to Ir) was not located, but its presence is indicated by a vacant octahedral position trans to C(35) of the carbonyl ligand. Careful inspection of the data establishes that molecules **a** and **b** possess identical coordination about the Ir center (*i.e.* they are the same geometrical isomer), that they do not differ significantly in rotational orientation of the PPh_3 group *vs* the geometry about the Ir center, that they differ only marginally in the skew conformation of the Si−CH_2−CH_2−P backbone of the chel unit, but that the Ph rings at P in the latter differ in their rotational relationship between the two molecules. Thus in molecule **a**, the plane of one Ph ring lies along the P(2)−Ir(1)−P(1) direction, with that of the other essentially orthogonal, *i.e.* flat on to the equatorial plane at Ir(1) that contains Cl(1), C(35), and Si(1), while in molecule **b**, although the Ph planes are again close to orthogonal, each approaches coplanarity with a bisector of the octahedral angles at Ir(2). These effects are defined by the relevant torsional angles (see Supporting Information).

There are minor distortions of bond angles toward the position of the hydride ligand, *i.e.* Si(1)−Ir(1)−Cl(1) = 164.3(3)° with P(1)−Ir(1)−P(2) = 171.2(3)°, possibly to accommodate the steric requirements of the chel and PPh_3 ligands. The Ir(1)−P(2) bond is shorter by about 0.04 Å *vs* Ir(1)−P(1), consistent with the chel P behaving as a stronger donor (alkyldiaryl- *vs* triarylphosphine) although the effect is slight. Of more interest are the Ir−Si and Ir−Cl bond lengths, at 2.41(1) and 2.503(8) Å, respectively. Despite the prolific development of Ir(III) chemistry, X-ray structural data for iridium−ligand bond distances are not abundant: however, sufficient detail exists to distinguish the impact of competing trans influences across the Ir center. Thus Ir−Cl distances trans to ligands that are respectively weak (*e.g.* Cl), intermediate (*e.g.* P), or strong (*e.g.* H) lie[18] in the following approximate ranges: 2.36−2.40, 2.42−2.45, and 2.50−2.52 Å. The long bond in compound **7** trans to Si is thus entirely consistent with the purported strong trans influence of silyl ligands.[14] The Si(1)−Ir(1)−P(2) angle, *i.e.* the "bite" angle of chel at Ir, is 84.1(4)°.

B. X-ray Crystal and Molecular Structure of Compound 8. A *cis*-Hydrido−Olefin Complex. Positional parameters are included in the Supporting Information; the molecular geometry is illustrated in Figure 2, where the vacant site trans to Cl gives away the position of the hydride ligand which was again not located. The Ir−Cl bond is therefore trans to H and, accordingly, is long[18] at 2.495(5) Å. The distances to the bound centers of the chel group are Ir−Si, 2.364(5), and Ir−P, 2.264(5) Å. The "bite" angle of the chel is 82.4(2)°, and the stronger ligand character of Si *vs* P is amply illustrated by the bond distances to the bound diolefin carbon atoms C(15), C(16), C(19), and C(20): the first two (2.35 Å; trans to Si) are longer by over 0.1 Å than those trans to P. At 2.23(2), 2.15(2) Å for Ir(1)−C(19) *vs* Ir(1)−C(20), the latter are also significantly different from one another, in a sense that is consistent with a slight twist of the cod framework that takes C(20) further away (156°) from a truly trans disposition with P than is C(19) (168°).

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Table 2. Ir−Ligand Bond[a] Distances (Å) in Silyliridium Compounds

compd	Ir−Si	Ir−P_{chel}	Ir−P	Ir−Cl
$Ir(chel)_2Cl$ **(6)**	2.31 (-)	2.30 (*P_{chel}*)		2.38 (-)
$IrH(chel)(CO)(PPh_3)Cl^b$ **(7)**	2.41 (*Cl*)	2.31 (*P*)	2.35 (*P_{chel}*)	2.51 (*Si*)
$IrH(chel)(cod)Cl^b$ **(8)**	2.36 (*C_{cod}*)	2.26 (*C_{cod}*)		2.50 (*H*)
$Ir(chel)(CO)_2(PPh_3)^c$	2.45 (*P*)	2.34 (-)	2.37 (*Si*)	
$IrH_2(chel)(CO)(PPh_3)^b$	2.39^d (*P*)	2.34^d (*H*)	2.37^d (*Si*)	
fac-$IrH(PMe_3)_3(Me)(SiEt_3)^{b,e}$	2.42 (*P*)		2.30 (*C_{Me}*) 2.34 (*H*) 2.36 (*Si*)	
$IrH(Si^iPr_2OH)(PEt_3)_2Cl^f$	2.31 (-)		2.29 (*P*)	2.42 (-)

[a] Atom trans to Ir−L bond shown italicized in parentheses. [b] Octahedral complex. [c] Ir(I) complex. [d] Unpublished data: Auburn, M. J.; Stobart, S. R.; Zawarotko, M. J., 1985. [e] See: Aizenberg, M.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 6456. [f] See: Goikhman, R.; Aizenberg, M.; Kraatz, H.; Milstein, D. *J. Am. Chem. Soc.* **1995**, *117*, 5865.

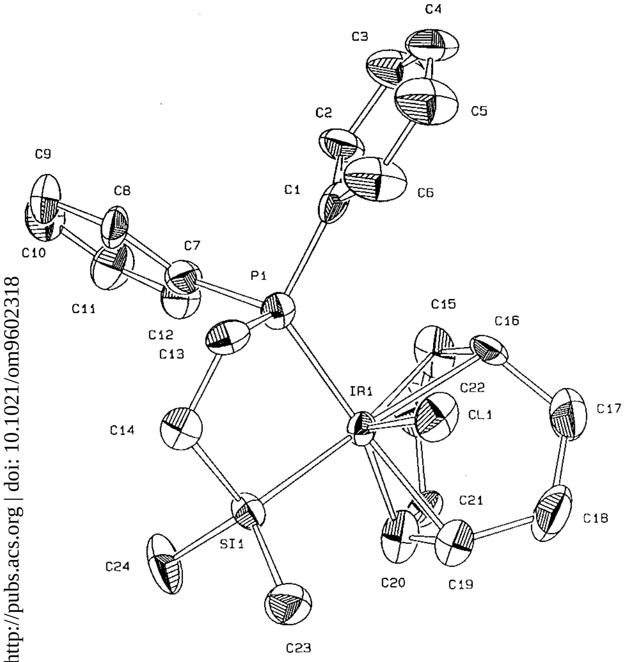

Figure 2. ORTEP plot of IrH(chel)(cod)Cl **(8)**. Selected distances (Å) and angles (deg): Ir(1)−Cl(1), 2.495(5); Ir(1)−P(1), 2.264(5); Ir(1)−Si(1), 2.364(5); Ir(1)−C(15), 2.352(13); Ir(1)−C(16), 2.35(2); Ir(1)−C(19), 2.23(2); Ir(1)−C(20), 2.15(2); Cl(1)−Ir(1)−P(1), 85.8(2); Cl(1)−Ir(1)−Si(1), 88.0(2); Cl(1)−Ir(1)−C(19), 82.5(4); Cl(1)−Ir(1)−C(20), 117.7(5); P(1)−Ir(1)−Si(1), 82.4(2); P(1)−Ir(1)−C(19), 168.2(4); P(1)−Ir(1)−C(20), 156.2(5); Si(1)−Ir(1)−C(19), 95.7(4); Si(1)−Ir(1)−C(20), 93.9(5).

C. X-ray Crystal and Molecular Structure of Compound 6: An Unusually Distorted Five-Coordinate d^6 Metal Center. Positional parameters are again listed in the Supporting Information; the molecular geometry is shown as Figure 3. Superficially the structure is TBP in character, with the two chel P atoms trans to one another in recognizably axial sites; an equatorial plane is defined by the two chel Si centers and the chloride ligand. The molecules are in fact propelloid, *i.e.* chiral possessing C_2 point group symmetry. The four bound atoms of the two chel ligands are virtually equidistant (2.3 Å) from Ir: P(1) at 2.313(7), P(2) at 2.293(7), Si(1) at 2.302(7), and Si(2) at 2.315(8) Å. The chel “bite” angles are 83.6(2), 84.3(3)°, and the dihedral angles between the pairs of planar Ph groups on P are 97, 101°. The remarkable features of the structure, however, are the bond angles in the equatorial plane: Si(1)−Ir(1)−Si(2) is only 86.3(3)°, despite the potential for unfavorable approach of silylmethyl hydrogens on opposing chel frameworks, while the two Si−Ir−Cl angles are 134.8(2), 138.9(2)°. At the same time the Ir−Cl distance of 2.381(6) Å is conspicuously *short* (not long, as was suggested[10] by us earlier) by comparison with those found in **7** and **8**.

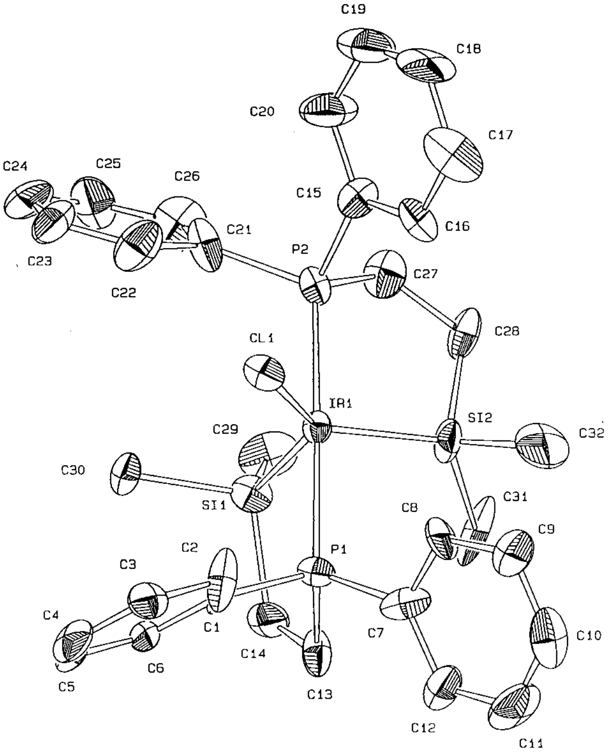

Figure 3. ORTEP plot of Ir(chel)$_2$Cl **(6)**. Selected distances (Å) and angles (deg): Ir(1)−Cl(1), 2.381(6); Ir(1)−P(1), 2.313(7); Ir(1)−P(2), 2.293(7); Ir(1)−Si(1), 2.302(7); Ir(1)−Si(2), 2.315(8); Si(1)−C(14), 1.90(3); Si(1)−C(29), 1.90(3); Si(1)−C(30), 1.92(3); Si(2)−C(28), 1.85(3); Si(2)−C(31), 1.93(3); Si(2)−C(32), 1.84(3); C1(1)−Ir(1)−P(1), 89.7(2); Cl(1)−Ir(1)−P(2), 91.1(2); C1(1)−Ir(1)−Si(1), 134.8(2); Cl(1)−Ir(1)−Si(2), 138.9(2); P(1)−Ir(1)−P(2), 178.3(2); P(1)−Ir(1)−Si(1), 83.6(2); P(1)−Ir(1)−Si(2), 96.1(2); P(2)−Ir(1)−Si(1), 94.8(2); P(2)−Ir(1)−Si(2), 84.3(3); Si(1)−Ir(1)−Si(2), 86.3(3).

Discussion

We focus on the irregularities that are evident in the structure of complex **6**. Some pertinent bond lengths are compared in Table 2. The data identify the Ir−Cl bond in the 5-coordinate Ir(III) complex as being shorter by over 0.1 Å than those trans to the strongly trans influencing centers in **7** or **8**. At the same time, while the axial bond lengths (*i.e.* to P) appear to be about normal, the Ir−Si distances are also contracted, by at least 0.05 Å *vs* those in the 6-coordinate complexes. The gross structure of **6**, which we concluded earlier[10] showed “no close relationship with either of the classic 5-coordinate stereochemistries”, is now recognizable as the dist-TBP geometry defined by Eisenstein *et al.*,[2,6] *i.e.* parallels that found in the Ir(III) analogues **1−3**. In compound **3**, the hydride ligands at Ir(III), which were located by using neutron diffraction, were found to subtend a narrow angle (73°) at Ir, resembling those between R, R′ (76°) and between H and Ph (78°) in **1** and **2**, respectively, as well as those between the two Ir−Si bonds (86°) in **6**. The Ir−Cl bond in **3**, at 2.410 Å, is[6] nearly as short as that in **6**, although the calculations[2] are equivocal about Ir−Cl bonding, rating Cl as weakly π-donating (compared with NH_2 or OR)[2] or as a poor π donor[6] and predicting[2] a bond (in the dist-TBP structure) substantially longer than that observed.

We believe that the short Ir−Cl bond distances in complexes **1−3** and **6** (or corresponding bonds in the small family of related molecules[2,4−6,8−12]) should not necessarily be taken as evidence for significant π-donor character[6] of the Cl atom in these systems: they appear contracted only when compared with bonds to Cl that are lengthened by occupation of a site trans to a strongly trans influencing ligand, like those in **7** or **8** (see Table 2). Indeed in the rhodium analogue $RhH_2Cl(P^iPr_3)_2$ of **1−3** and **6**, which is[11] of type **B**, the Rh−Cl bond at 2.422(1) Å is actually very *long* compared with that (2.324 Å) in $RhHCl_2(P^iPr_3)_2$ (where Cl is trans to a weak Cl center in a geometry of type **A**). Thus it is evident that, in compound **6**, all three $M{-}L_{eq}$ bonds are contracted because none of the three *eq* atoms is in direct competition for orbital overlap, and this is in accordance with the general observation that in regular TBP structures $M{-}L_{eq}$ distances are typically shorter than corresponding $M{-}L_{ax}$ bonds.[19]

Experimental data support the idea that silyl ligands exert among the strongest of trans influences across a metal center,[10,14] so that Si−M bonds will themselves be least susceptible to lengthening by competition for orbital overlap. Any contraction of Si−M bond distances from established ranges should therefore be definitive (unlike similar changes in M−Cl, which because of the weak influence of chloride is effectively merely lengthened less as the strength of the trans ligand decreases). Accordingly, identification as short of *eq* bonds between M and strongly trans-influencing *eq* groups (those separated by the narrow angle α of ref 2) in the new dist-TBP structures is especially significant. The Ir−Si *eq* bonds in complex **6** are clearly short, *q.v.* (Table 2): whether or not this can be related to π-effects requires further consideration.

It is appropriate to discuss the Ir−Si bonding in complex **6** in terms similar to those applied earlier[2,6] to the equatorial Ir−Cl interaction in **3**. Thus the silyl centers are also potential π-donors (*via* interaction of a filled SiC_3 σ bonding level with the LUMO): this is favored *vs* Cl by electronegativity differences, but the effect is predicted to be weak (like Cl) because of poor overlap.[20] What remains to be considered is possible π-acceptor behavior of the silyl group, with donation from a filled Ir d_π orbital either into a SiC_3 antibonding level (σ*) or into a vacant Si 3d orbital.[21] The first of these alternates is unlikely to be significant, again because of poor overlap, while what experimental evidence there is militates against the second.[21] Similar arguments pertain to *eq* Ru−P bonding in the cation[12a] $Ru(diphos)_2Cl^+$. Electron delocalization away from the Ir atom in **6** is in any case at odds with the view of the latter as electron deficient (16e Ir^{III}); if it was in fact important, it would be expected to operate more strongly in silyls of 16e Ir^{I} or 18e Ir^{III}, whereas in both these situations significantly longer Ir−Si bonds are found (Table 2).

In conclusion, while the orientation effects observed[6] with O- and N-bound ligands (for which better L−M orbital overlap would be anticipated *vs* Cl) at Ir are interesting, accommodation of strong σ-donor capacity of *eq* ligands by a disposition that minimizes the effect of competing trans influences seems sufficient to account for short *eq* bond lengths; the relative importance of π-bonding in **6** (as well as in **1−3**) is likely to be minor. Indeed it seems likely that strong π interactions of the type suggested[6] earlier might inhibit nucleophile approach[20a] to the metal vicinity in **6** or its relatives, contrary to the pattern of reactivity that is seen.[6,10]

Experimental Section

Isolation of the three complexes **(6−8)**, as crystalline materials that were respectively colorless, ivory-colored, or chrome-yellow, has been described previously.[10,13] Crystal suitable for X-ray diffraction were obtained from ether/hexane (**6**, as well-formed blocks) or cold ether (**7** or **8**, as platelets) and were mounted in glass capillaries. Crystal data for the three compounds are collected in Table 1; as is evident from the latter, data collection, structure solution, and refinement followed parallel procedures throughout. Unit cell parameters were obtained by least squares on the setting angles for 24 **(6)**, 21 **(7)**, or 25 **(8)** reflections in the respective ranges $20.00 < 2\theta < 24.00°$, $20.00 < 2\theta < 28.00°$, and $7.60 < 2\theta < 44.25°$. In each case intensities of 3 representative reflections measured every 150 reflections remained constant throughout. Empirical absorption corrections were applied using the program DIFABS, and data were corrected for Lorentz and polarization effects.[22]

The structures were solved by direct methods. Refinement was by least squares. Non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in their geometrically calculated positions with a distance of 1.08 Å, kept fixed during final refinement, and assigned $B_H = 1.2B_{\text{bonded atom}}$. For compound **8** the C(21) and C(22) atoms of the 1,5-cyclooctadiene unit are (0.57:0.43)% disordered (C(21), C(21* and C22, C(22)*). Full details are provided in the Supporting Information.

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Supporting Information Available: Text describing complete X-ray experimental details, PLUTO and ORTEP plots, and tables of fractional atomic coordinates, hydrogen atom positional parameters, isotropic and anisotropic temperature factors, interatomic distances, interbond angles, torsional angles for compounds **6−8**, and least-squares planes for **6** and **8** (64 pages). Ordering information is given on any current masthead page.

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