

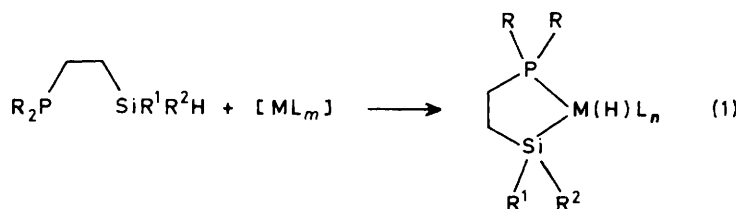
**Phosphinoalkylsilyl Complexes. Part 7.<sup>1</sup> Synthesis and Reactivity of Octahedral, Bis(chelate)dicarbonyl Complexes of Ruthenium(II) and Osmium(II). Conformational Properties of the Bis(chelate) Framework and X-Ray Crystal Structures of  $[M(PPh_2CH_2CH_2SiMe_2)_2(CO)_2]$  ( $M = Ru$  or  $Os$ )<sup>†</sup>**

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Reaction of the phosphinoethylsilanes  $Ph_2PCH_2CH_2SiR^1R^2H$  ( $R^1 = R^2 = Me$  or  $Ph$ ;  $R^1 = Me$ ,  $R^2 = Ph$ ) with  $[M_3(CO)_{12}]$  ( $M = Ru$  or  $Os$ ) at  $140^\circ C$  affords the octahedral complexes  $[M(PPh_2CH_2CH_2SiR^1R^2)_2(CO)_2]$  for which i.r. and n.m.r. data suggest a common structure with *trans* CO groups. The Ru complex in which  $R^1 = R^2 = Me$  is chemically inert, failing to undergo carbonyl displacement or to show evidence for either nucleophilic or electrophilic attack on co-ordinated CO [a characteristic which can be correlated with the low energy of  $\nu(CO)$  (*ca.*  $1920\text{ cm}^{-1}$ ) and which may result from inductive electron release from Si onto Ru], but reacting in boiling  $CCl_4$  or with HCl gas or  $I_2$  with cleavage of both Ru–Si bonds. The crystal and molecular structure of the Os complex in which  $R^1 = R^2 = Me$  has been determined by X-ray diffraction, showing that the chelate ligands adopt a *cis* relationship in the equatorial plane; in this structure two conformers coexist in the crystal, distinguished by the arrangement of the chelate ligand methylene backbones which are either parallel or skew with respect to one another. The crystals are triclinic, space group  $P\bar{1}$ , with  $a = 12.598(3)$ ,  $b = 17.228(4)$ ,  $c = 18.501(4)$  Å,  $\alpha = 119.96(2)$ ,  $\beta = 101.39(2)$ ,  $\gamma = 90.36(1)^\circ$ , and  $Z = 4$ . Mean M–Si and M–P distances are *ca.* 2.48 and 2.38 Å respectively, the latter conspicuously long compared with related compounds and consistent with the strongly *trans*-influencing behaviour of Si.

Earlier papers in this series<sup>1–4</sup> have described co-ordination to platinum, rhodium, or iridium centres *via* 'chelate-assisted' hydrosilylation of (2-diphenylphosphinoethyl)dimethylsilane<sup>5</sup> ( $Ph_2PCH_2CH_2SiMe_2H$ ) and related compounds [equation (1)]. Access to a corresponding bridging geometry incorporating

$[M = Ru$  (3) or  $Os$  (4)] which are formed when the silane  $Ph_2PCH_2CH_2SiMe_2H$  is allowed to react with  $[M_3(CO)_{12}]$ . Analogues (5)–(8) of compounds (3) and (4) have also been isolated by using the precursors<sup>5</sup>  $Ph_2PCH_2CH_2SiR^1R^2H$  ( $R^1 = R^2 = Ph$ ;  $R^1 = Me$ ,  $R^2 = Ph$ ).



the  $\mu$ -(2-diphenylphosphinomethyl)dimethylsilyl ligand has also been established: the binuclear complexes  $[M_2(\mu-PPh_2CH_2SiMe_2)_2(CO)_6]$  [ $M = Ru$  (1) or  $Os$  (2)] have been isolated<sup>6</sup> from reactions of  $Ph_2PCH_2SiMe_2H$  with  $[M_3(CO)_{12}]$ . In a preliminary account<sup>2</sup> we commented briefly on the structural relationship between the chelating silyl ligand  $Ph_2PCH_2CH_2SiMe_2-$  and the familiar chelating diphosphine, 1,2-bis(diphenylphosphino)ethane (dppe,  $Ph_2PCH_2CH_2PPh_2$ ), which is isoelectronic with  $Ph_2PCH_2CH_2SiMe_2H$ , and on the stereochemical consequences of chirality at Si in planar arrangements of the type *cis*- $[Pt(PPh_2CH_2CH_2SiR^1R^2)_2]$ . In the present paper these ideas are developed further in relation to the octahedral complexes  $[M(PPh_2CH_2CH_2SiMe_2)_2(CO)_2]$

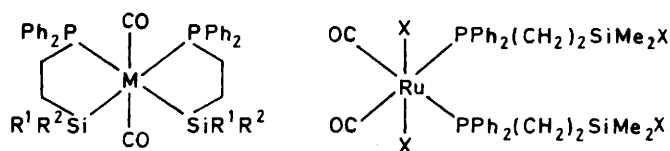
### Experimental

**General.**—All synthetic manipulations were carried out using standard inert-atmosphere techniques and all solvents were dried and distilled under dry dinitrogen gas. N.m.r. spectra were obtained with Perkin-Elmer R32 ( $^1H$ , 90 MHz) or Nicolet TT-14 ( $^{31}P$ , 24.3 MHz) spectrometers and i.r. spectra were recorded using a Perkin-Elmer 283 spectrophotometer (Table 1). The synthetic route to the phosphinoethylsilanes  $Ph_2PCH_2CH_2SiR^1R^2H$  ( $R^1 = R^2 = Me$  or  $Ph$ ;  $R^1 = Me$ ,  $R^2 = Ph$ ) has been described elsewhere.<sup>5</sup>

**Synthesis of Compounds.**—Dicarbonylbis[(2-diphenylphosphinoethyl)dimethylsilyl]ruthenium(II), (3). Tetrahydrofuran (thf, 3 cm<sup>3</sup>),  $[Ru_3(CO)_{12}]$  (32 mg, 0.05 mmol), and  $Ph_2PCH_2CH_2SiMe_2H$  (90 mg, 0.33 mmol) were loaded under a  $N_2$  atmosphere into a Carius tube, which was then cooled to  $-196^\circ C$ , evacuated, and sealed. After heating for 72 h at  $140^\circ C$  the tube was opened, affording a pale yellow solution from which volatiles were removed to give a white solid. After

<sup>†</sup> Dicarbonylbis[(2-diphenylphosphinoethyl)dimethylsilyl-*PSi*]-ruthenium and -osmium.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.



- (3; M = Ru, R<sup>1</sup> = R<sup>2</sup> = Me) (9; X = Cl)  
 (4; M = Os, R<sup>1</sup> = R<sup>2</sup> = Me) (10; X = I)  
 (5; M = Ru, R<sup>1</sup> = R<sup>2</sup> = Ph)  
 (6; M = Os, R<sup>1</sup> = R<sup>2</sup> = Ph)  
 (7; M = Ru, R<sup>1</sup> = Me, R<sup>2</sup> = Ph)  
 (8; M = Os, R<sup>1</sup> = Me, R<sup>2</sup> = Ph)

redissolving in the minimum of CH<sub>2</sub>Cl<sub>2</sub> and addition of an equal volume of heptane, cooling to -30 °C resulted in slow deposition of the white, crystalline product (39 mg, 0.06 mmol, 37%), m.p. 224–225 °C (Found: C, 58.35; H, 5.90. Calc. for C<sub>34</sub>H<sub>40</sub>O<sub>2</sub>P<sub>2</sub>RuSi<sub>2</sub>: C, 58.35; H, 5.70%). Prolonged refrigeration of the mother-liquor afforded a second crop of crystals (10 mg).

*Dicarbonylbis*[(2-diphenylphosphinoethyl)dimethylsilyl]-osmium(II), (4). In a sealed, evacuated Carius tube [Os<sub>3</sub>(CO)<sub>12</sub>] (86 mg, 0.095 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>H (155 mg, 0.57 mmol) were heated together at 145 °C. After 48 h off-white crystals were present and the tube was opened and washed out with dry Et<sub>2</sub>O (15 cm<sup>3</sup>). Evaporation of solvent yielded white microcrystals of the product (78 mg, 0.10 mmol, 35%), m.p. 230–231 °C, which were washed with pentane (Found: C, 51.55; H, 5.35. Calc. for C<sub>34</sub>H<sub>40</sub>O<sub>2</sub>OsP<sub>2</sub>Si<sub>2</sub>: C, 51.75; H, 5.10%). Crystals (m.p. 235 °C) suitable for X-ray diffraction were grown from diethyl ether-pentane solution at -30 °C.

*Dicarbonylbis*[(2-diphenylphosphinoethyl)diphenylsilyl]-ruthenium(II), (5). A similar sealed-tube reaction (48 h, 165 °C) between [Ru<sub>3</sub>(CO)<sub>12</sub>] (160 mg, 0.25 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>-SiPh<sub>2</sub>H (600 mg, 1.52 mmol) was followed by dissolution in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) then evaporation to dryness to yield a brownish solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-heptane afforded the pale fawn-coloured product (330 mg, 0.35 mmol, 46%), m.p. 224–225 °C (Found: C, 68.1; H, 5.05. Calc. for C<sub>52</sub>H<sub>48</sub>O<sub>2</sub>P<sub>2</sub>RuSi<sub>2</sub>: C, 68.4; H, 5.10%).

*Dicarbonylbis*[(2-diphenylphosphinoethyl)diphenylsilyl]-osmium(II), (6). On heating [Os<sub>3</sub>(CO)<sub>12</sub>] (12 mg, 0.013 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiPh<sub>2</sub>H (21 mg, 0.053 mmol) at 145 °C for 48 h in a sealed evacuated tube a white crystalline mass formed: after opening the tube this was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) and filtered. Heptane (3 cm<sup>3</sup>) was added to the solution and the volume of the mixture was reduced by careful evacuation until solid just started to deposit. Redissolution by addition of CH<sub>2</sub>Cl<sub>2</sub> (0.3 cm<sup>3</sup>) was followed by cooling to -30 °C, resulting in very slow formation (1 week) of white crystals of the product (two crops yielded 10 mg, ca. 40%), m.p. >325 °C (decomp.), as the dichloromethane solvate (Found: C, 58.4; H, 4.45. Calc. for C<sub>52</sub>H<sub>48</sub>O<sub>2</sub>OsP<sub>2</sub>Si<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 58.85; H, 4.45%).

*Dicarbonylbis*[(2-diphenylphosphinoethyl)(methyl)phenylsilyl]ruthenium(II), (7). Reaction for 30 h at 140 °C in a sealed, evacuated tube between [Ru<sub>3</sub>(CO)<sub>12</sub>] (64 mg, 0.10 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiMePhH (200 mg, 0.60 mmol) yielded an off-white solid (74 mg, 35%). Examination of this crude material using n.m.r. spectroscopy showed two signals (ca. 3:2 ratio) due to δ(SiMe) in the <sup>1</sup>H spectrum and also two <sup>31</sup>P resonances separated by ca. 0.5 p.p.m., consistent with formation of a diastereoisomeric mixture. Subsequent recrystallization at -30 °C from heptane-CH<sub>2</sub>Cl<sub>2</sub> (1:1) slowly gave white crystals of the product, m.p. ca. 280 °C (decomp.) (Found: C, 63.6; H, 5.55. Calc. for C<sub>44</sub>H<sub>44</sub>O<sub>2</sub>P<sub>2</sub>RuSi<sub>2</sub>: C, 64.15; H, 5.35%). Successive cropping of the crystalline complex was used to

separate in a pure state the less soluble diastereoisomer, shown by n.m.r. spectroscopy (Table 1) to be the more abundant constituent of the crude reaction product. The less abundant, more soluble isomer could not be successfully purified out of CH<sub>2</sub>Cl<sub>2</sub>-heptane solvent; other methods of diastereomer separation were not attempted.

*Dicarbonylbis*[(2-diphenylphosphinoethyl)(methyl)phenylsilyl]osmium(II), (8). From a reaction similar to that described for (7) (24 h, 140 °C), between [Os<sub>3</sub>(CO)<sub>12</sub>] (77 mg, 0.09 mmol) and Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>SiMePhH (170 mg, 0.51 mmol), was isolated from CH<sub>2</sub>Cl<sub>2</sub> solution a pale yellow solid. This was shown by <sup>1</sup>H and <sup>31</sup>P n.m.r. spectroscopy to be a diastereoisomeric mixture, of which only the less soluble component (see Table 1) could be obtained pure (100 mg, 43%) by fractional crystallization from CH<sub>2</sub>Cl<sub>2</sub>-heptane mixtures, m.p. (less soluble diastereoisomer) 316–318 °C (Found: C, 58.1; H, 5.05. Calc. for C<sub>44</sub>H<sub>44</sub>O<sub>2</sub>OsP<sub>2</sub>Si<sub>2</sub>: C, 57.9; H, 4.80%).

*Reactions of Compound (3).*—With CCl<sub>4</sub>. Complex (3) (50 mg, 0.07 mmol) was refluxed in CCl<sub>4</sub> for 4 h, during which time the solution gradually became yellow. Evaporation to dryness followed by thorough washing with Et<sub>2</sub>O afforded the product (47%) as a pale yellow powder (Found: C, 49.2; H, 4.2. Calc. for C<sub>34</sub>H<sub>40</sub>Cl<sub>4</sub>O<sub>2</sub>P<sub>2</sub>RuSi<sub>2</sub>: C, 48.5; H, 4.75%). I.r. (KBr): ν(CO), 2 050 vs, 1 998 vs cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>), δ 7.76–7.41 (20 H, Ph), 2.88–1.80 (4 H, -CH<sub>2</sub>P), 0.90–0.20 (4 H, -CH<sub>2</sub>Si), 0.09 (12 H, -SiMe<sub>2</sub>); <sup>31</sup>P (CD<sub>2</sub>Cl<sub>2</sub>), δ [vs. P(OMe)<sub>3</sub>] -116.2.

*With HCl.* Hydrogen chloride gas was bubbled slowly through a stirred solution of compound (3) (50 mg, 0.074 mmol) in methylene chloride (10 cm<sup>3</sup>) at ca. 50 °C for 6 h. The resulting yellow solution was pumped to dryness, washed with diethyl ether, and collected as a yellow powder (45%) identical to that obtained above.

*With I<sub>2</sub>.* Compound (3) (50 mg, 0.07 mmol) was dissolved in thf (15 cm<sup>3</sup>). A solution of I<sub>2</sub> (36 mg, 0.14 mmol) in thf (5 cm<sup>3</sup>) was added dropwise over 30 min, then the mixture was stirred (20 °C). No reaction had taken place after 22 h (n.m.r. spectroscopy) so the mixture was heated at 70 °C for 18 h. The yellow product (34%) was recovered as above (Found: I, 40.0. Calc. for C<sub>34</sub>H<sub>40</sub>I<sub>4</sub>O<sub>2</sub>P<sub>2</sub>RuSi<sub>2</sub>: I, 42.0%). I.r. (KBr): ν(CO), 2 040 vs, 1 995 vs cm<sup>-1</sup>. N.m.r.: <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>), δ 7.68–7.40 (20 H, Ph), 2.60–2.50 (4 H, -CH<sub>2</sub>P), 0.40–0.08 (4 H, -CH<sub>2</sub>Si), -0.08 (12 H, SiMe<sub>2</sub>); <sup>31</sup>P (CD<sub>2</sub>Cl<sub>2</sub>), δ [vs. P(OMe)<sub>3</sub>] -128.0.

*X-Ray Crystallography.*—Data collection and refinement for compounds (3) and (4). General procedures have been described previously.<sup>1,2,6</sup> Crystal data for the osmium complex (4) are listed in Table 2. A crystal of the ruthenium analogue (3) was also examined; although it diffracted poorly it was shown by a partial refinement of the data to be isostructural with crystals of (4). The data were collected using an Enraf-Nonius CAD4 four-circle diffractometer; Lorentz polarization corrections were applied but an absorption correction was not attempted because of irregularity in the crystal shape. The unit cell for compound (4) contained pairs of two non-equivalent molecules and the structure was solved by Patterson and Fourier methods using SHELX 76,<sup>7</sup> with refinement by large-block least-squares methods using  $w = (\sigma^2 F + 0.004 513 F^2)^{-1}$  to  $R = 0.046$  with  $R' = 0.0458$  (see Table 2). Only the Os, P, and Si atoms were refined anisotropically. Hydrogen atoms were not located. The final difference map showed no maximum greater than 0.8 e Å<sup>-3</sup>. Final fractional atomic co-ordinates are listed in Table 3. Important bond distances and angles are collected in Table 4.

## Results and Discussion

Reaction at elevated temperature (typically 140 °C) between [M<sub>3</sub>(CO)<sub>12</sub>] (M = Ru or Os) and the phosphinoethylsilanes<sup>5</sup>

**Table 1.** Infrared<sup>a</sup> and n.m.r. data

Compound	$\nu(\text{CO})/\text{cm}^{-1}$	$^1\text{H}$ n.m.r. <sup>b</sup>	$^{31}\text{P}$ n.m.r. <sup>c</sup>
(3)	1 996m, 1 922vs, 1 913vs	0.36 <sup>d</sup>	-85.2
(4)	1 997m, 1 993m, 1 914vs, 1 907vs <sup>e</sup>	0.38 <sup>f,g</sup>	-118.0
(5)	1 938vs		-82.7
(6)	1 931vs		-120.9
(7)	2 001w, 1 929vs	-0.96	-81.5
(8)	2 002w, 1 923vs	0.00	-114.2

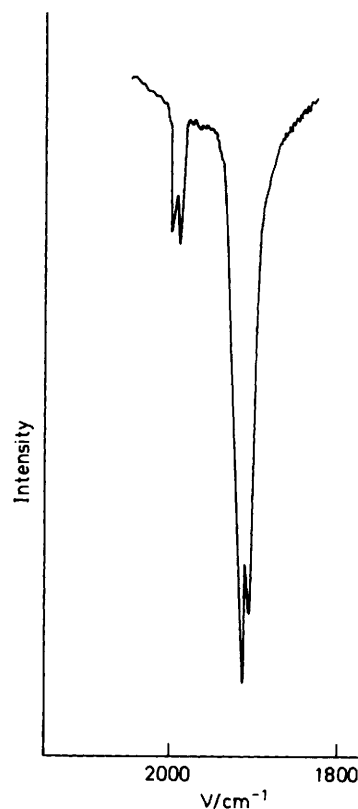
<sup>a</sup> KBr pellet. <sup>b</sup> 90 MHz in  $\text{CDCl}_3$  solution,  $\delta/\text{p.p.m.}$  vs. internal  $\text{SiMe}_4$ .  $\text{SiCH}_3$  protons; in all spectra multiplets in the ranges  $\delta$  0.4–2.4 and 7.0–7.5 were observed attributable to  $\text{CH}_2$  and Ph protons respectively. <sup>c</sup> 24.3 MHz in  $\text{CDCl}_3$  solution,  $\delta/\text{p.p.m.}$  vs. external  $\text{P}(\text{OMe})_3$ . <sup>d</sup> At 250 MHz the  $\text{SiCH}_2$  and  $\text{PCH}_2$  signals were recognizable as the  $A_2$  and  $B_2$  parts of an  $A_2B_2X$  pattern centred at  $\delta$  0.7 and 2.37 respectively (see ref. 5). <sup>e</sup> 2 005m and 1 927vs  $\text{cm}^{-1}$  in methylocyclohexane solution. <sup>f</sup> At 250 MHz:  $\text{SiCH}_2$ ,  $\delta$  0.66;  $\text{PCH}_2$ ,  $\delta$  2.39. <sup>g</sup>  $^4J(\text{PH}) = 0.73$  Hz.

**Table 2.** Crystal data and summary of intensity data collection and structure refinement for compound (4)

Formula	$\text{C}_{34}\text{H}_{40}\text{O}_2\text{OsP}_2\text{Si}_2$
<i>M</i>	788.96
Crystal dimensions (mm)	0.25 × 0.30 × 0.30
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> /Å	12.598(3)
<i>b</i> /Å	17.228(4)
<i>c</i> /Å	18.501(4)
$\alpha$ /°	119.96(2)
$\beta$ /°	101.39(2)
$\gamma$ /°	90.36(1)
<i>U</i> /Å <sup>3</sup>	3 384.2
<i>Z</i>	4
<i>D</i> <sub>c</sub> /g cm <sup>-3</sup>	1.564
Radiation ( $\lambda$ /Å)	$\text{Mo-K}\alpha$ (0.710 69)
2 $\theta$ Range (°)	4–46
Data collected	6 295
Data with <i>I</i> > $\sigma(I)$	5 430
<i>F</i> (000)	1 576
Final <i>R</i>	0.046
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	37.80

$\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiR}^1\text{R}^2\text{H}$  ( $\text{R}^1 = \text{R}^2 = \text{Me}$  or  $\text{Ph}$ ;  $\text{R}^1 = \text{Me}$ ,  $\text{R}^2 = \text{Ph}$ ) in sealed, evacuated reaction tubes yielded a family of complexes for which analytical data were consistent with the formulation  $[\text{M}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiR}^1\text{R}^2)_2(\text{CO})_2]$ . These new products, (3)–(8), which were obtained in moderate yields as white, high-melting, air-stable crystalline solids, were further characterized by i.r. measurements and  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy (see Table 1). In the n.m.r. spectra of each of the complexes (7) and (8), derived from prochiral silanes, two silyl-methyl proton signals were resolved in unequal ratio and correspondingly two  $^{31}\text{P}$  chemical shifts were distinguishable; this is attributable<sup>2,3</sup> to formation in each case of diastereoisomeric mixtures. Separation of these latter by fractional crystallization afforded as pure compounds the more abundant, less soluble components (see Experimental section); purification of the minor diastereomers was not pursued.

The i.r. spectra of complexes (3)–(8) each contain sharp, intense absorptions identifiable as CO stretching vibrations, in addition to complex contours due to vibrations<sup>5</sup> of the  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiR}^1\text{R}^2$  ligands. For compounds (5) and (6) only single  $\nu(\text{CO})$  bands were evident, as was found by Mawby and co-workers<sup>8</sup> for all-*trans* isomers of  $[\text{Ru}(\text{CO})_2(\text{PMe}_2\text{Ph})_2\text{Cl}_2]$  and similar complexes; however, compared with these

**Figure 1.** Infrared spectrum (solid state, KBr pellet) of  $[\text{Os}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)_2(\text{CO})_2]$  (4) in the carbonyl stretching region

complexes, in which  $\nu(\text{CO})$  absorptions were in the range 1 997–2 033  $\text{cm}^{-1}$ , a substantial lowering in energy to 1 938 and 1 931  $\text{cm}^{-1}$  respectively is evident (Table 1). While silyl ligands are regarded as being powerfully electron-releasing towards transition-metal centres<sup>9</sup> the observed decrease in  $\nu(\text{CO})$  must be associated primarily with equatorial phosphine substitution, because in *cis*- $[\text{Fe}(\text{CO})_4(\text{SiMe}_3)_2]$  and its disilyl chelate relative  $[\text{Fe}(\text{CO})_4(\text{SiMe}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)]$   $\nu(\text{CO})$  absorptions are centred<sup>10</sup> nearer 2 000  $\text{cm}^{-1}$ . Conjunction of a *trans*-dicarbonyl disposition with equatorial co-ordination exclusively by more basic ligating groups in an octahedral geometry is relatively uncommon, but an example is provided by the product of iodine oxidation of *cis*- $[\text{Mo}(\text{CO})_2(\text{dppe})_2]$ . Indeed in the corresponding chromium chemistry,<sup>11a</sup> where both species have been assigned a *trans* geometry, the complexes  $[\text{Cr}(\text{CO})_2(\text{dppe})_2]^{n+}$  show single  $\nu(\text{CO})$  bands at extraordinarily low energy (1 780  $\text{cm}^{-1}$ ,  $n = 0$ ; 1 838  $\text{cm}^{-1}$ ,  $n = 1$ ) although the significance of the values has not been assessed in electronic terms. A *cis* geometry has been claimed for<sup>11b</sup> the paramagnetic neutral analogue  $[\text{Re}(\text{CO})_2(\text{dppe})_2]$ , which shows two  $\nu(\text{CO})$  fundamentals at 1 860 and 1 920  $\text{cm}^{-1}$ .

For the methylsilyl analogues (3) and (4) a second, weaker absorption was discernible above 2 000  $\text{cm}^{-1}$  in solution, Table 1 (although a *trans*-dicarbonyl structure has been confirmed crystallographically for both species); similar weak high-energy  $\nu(\text{CO})$  components were observed for compounds (7) and (8). The symmetric stretching vibration of a *trans*-dicarbonyl unit in an octahedral configuration may be rendered i.r.-active either by distortion of equatorial planarity or by departure of the  $\text{M}(\text{CO})_2$  axis from linearity. Since both such effects are evident in the crystal structure of the osmium compound (4) it is not surprising that  $\nu_{\text{sym}}(\text{CO})$  gains sufficient intensity to be

**Table 3.** Fractional atomic co-ordinates ( $\times 10^5$  for Os,  $\times 10^4$  for others) for compound (4)\*

Molecule 1			Molecule 2				
Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Os(1)	46 191(3)	30 634(3)	24 686(3)	Os(2)	1 933(3)	70 753(3)	26 456(3)
C(1)	5 180(11)	2 342(9)	1 511(9)	C(3)	-86(9)	7 886(8)	3 701(8)
O(1)	5 640(9)	1 937(7)	956(7)	O(3)	-322(8)	8 346(6)	4 379(6)
C(2)	4 355(9)	4 100(8)	3 437(8)	C(4)	169(10)	6 003(9)	1 610(8)
O(2)	4 216(8)	4 780(7)	4 021(6)	O(4)	124(8)	5 290(7)	982(6)
P(1)	5 069(2)	2 178(2)	3 117(2)	P(3)	-112(3)	7 843(2)	1 872(2)
C(11)	4 151(9)	2 016(8)	3 688(8)	C(31)	841(10)	7 786(8)	1 228(8)
C(12)	3 362(10)	1 268(8)	3 261(8)	C(32)	678(12)	7 144(10)	368(9)
C(13)	2 556(13)	1 178(11)	3 670(10)	C(33)	1 465(14)	7 114(12)	-84(11)
C(14)	2 623(20)	1 855(17)	4 529(16)	C(34)	2 382(19)	7 711(16)	318(15)
C(15)	3 388(13)	2 565(11)	4 943(10)	C(35)	2 575(15)	8 368(12)	1 179(12)
C(16)	4 181(11)	2 680(9)	4 550(9)	C(36)	1 787(13)	8 395(11)	1 639(10)
C(17)	5 347(13)	1 025(11)	2 442(10)	C(37)	-315(10)	9 031(8)	2 398(8)
C(18)	4 763(12)	535(10)	1 600(9)	C(38)	-564(11)	9 462(9)	3 197(9)
C(19)	4 905(13)	-391(11)	1 070(11)	C(39)	-805(13)	10 361(11)	3 592(10)
C(110)	5 684(13)	-755(11)	1 408(10)	C(310)	-729(14)	10 837(12)	3 166(11)
C(111)	6 316(14)	-257(12)	2 219(11)	C(311)	-514(15)	10 426(13)	2 370(12)
C(112)	6 162(20)	628(16)	2 759(16)	C(312)	-317(12)	9 501(10)	1 958(10)
Et(1)	6 354(12)	2 721(10)	3 957(9)	Et(5)	-1 434(12)	7 348(10)	1 077(10)
Et(2)	7 180(11)	2 957(9)	3 540(9)	Et(6)	-2 306(12)	7 321(10)	1 555(9)
Si(1)	6 553(3)	3 707(2)	3 147(2)	Si(3)	-1 822(3)	6 732(2)	2 181(2)
Me(1)	6 869(13)	4 868(11)	4 165(10)	Me(5)	-2 394(14)	5 502(12)	1 434(11)
Me(2)	7 375(13)	3 777(11)	2 433(11)	Me(6)	-2 624(13)	7 190(11)	3 062(11)
P(2)	2 741(2)	2 522(2)	1 755(2)	P(4)	2 135(2)	7 365(2)	3 153(2)
C(21)	1 721(9)	2 745(8)	2 394(8)	C(41)	3 038(10)	7 237(8)	2 450(8)
C(22)	2 032(11)	3 124(9)	3 275(9)	C(42)	2 836(12)	6 464(10)	1 641(10)
C(23)	1 228(11)	3 275(10)	3 755(9)	C(43)	3 566(13)	6 296(11)	1 100(11)
C(24)	130(12)	3 055(10)	3 334(9)	C(44)	4 446(14)	6 911(12)	1 372(11)
C(25)	-173(12)	2 678(10)	2 463(10)	C(45)	4 649(14)	7 674(12)	2 143(12)
C(26)	600(10)	2 512(9)	1 977(8)	C(46)	3 958(12)	7 836(10)	2 703(9)
C(27)	2 366(10)	1 325(8)	953(8)	C(47)	2 685(9)	8 463(8)	4 115(8)
C(28)	1 768(11)	746(9)	1 086(9)	C(48)	3 681(10)	8 583(9)	4 676(8)
C(29)	1 553(12)	-181(10)	471(9)	C(49)	4 087(13)	9 444(11)	5 400(10)
C(210)	1 932(15)	-535(12)	-283(12)	C(410)	3 503(14)	10 167(12)	5 547(11)
C(211)	2 509(14)	39(12)	-421(11)	C(411)	2 517(13)	10 046(11)	4 984(10)
C(212)	2 757(11)	979(9)	206(9)	C(412)	2 110(11)	9 189(9)	4 258(9)
Et(3)	2 252(12)	3 042(10)	1 125(9)	Et(7)	2 615(10)	6 535(9)	3 468(8)
Et(4)	2 788(11)	4 033(9)	1 605(9)	Et(8)	1 818(11)	6 428(9)	3 968(9)
Si(2)	4 336(3)	4 060(2)	1 863(2)	Si(4)	373(3)	6 130(2)	3 319(2)
Me(3)	4 952(12)	5 274(10)	2 553(10)	Me(7)	211(11)	4 854(10)	2 527(9)
Me(4)	4 748(13)	3 667(11)	809(11)	Me(8)	-534(14)	6 254(12)	4 076(11)

\* Me(*n*) represent the silyl methyl groups, and Et(*n*) the methylene carbons of the chelate ligand.

observed. I.r. spectra of KBr pellets prepared from microcrystalline samples of complex (4) showed further splitting of each  $\nu(\text{CO})$  band (Figure 1); a rationale for this observation is provided by the X-ray study described below which has established the coexistence of two quite different conformational isomers in the crystal.

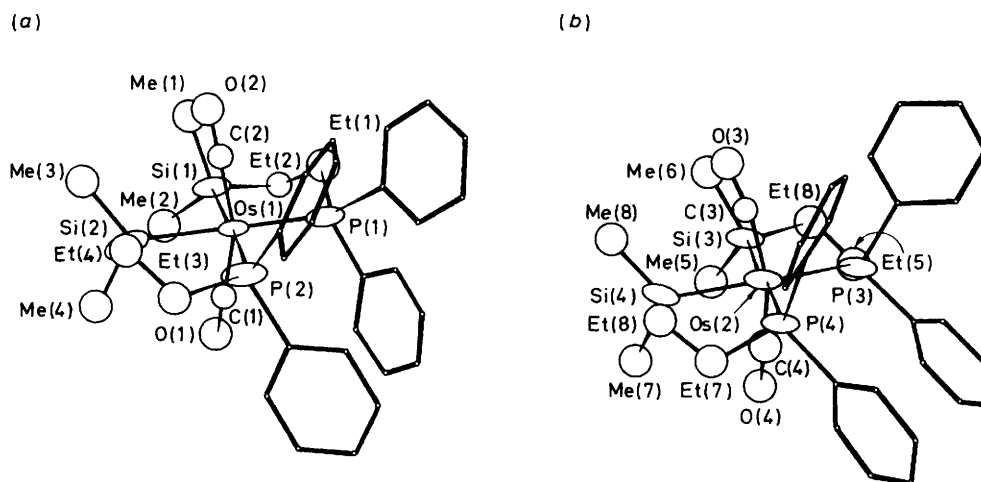
The spectroscopic data of Table 1 are indicative of a common geometry for the analogues (3)–(8) which corresponds to the stereochemical arrangement shown. Using chemical<sup>2</sup> and also crystallographic<sup>12</sup> methods, we have identified the more abundant diastereomer formed on oxidation of Pt<sup>0</sup> to [Pt(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMePh)<sub>2</sub>] as the racemic form (enantiomeric, C<sub>2</sub> symmetry), in which Ph groups at Si are disposed so as to avoid one another: *i.e.* for this bis(chelate) Pt<sup>II</sup> species the relationship of n.m.r. parameters (<sup>1</sup>H and <sup>31</sup>P) for *meso* and racemic isomers is known. A comparison of chemical shift values observed for these latter with those measured for the crude isomeric mixtures [M(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMePh)<sub>2</sub>(CO)<sub>2</sub>] suggested that the major (isolated) diastereomers (7) and (8) may also be the racemic modification. Recovery of the products (3)–(8) as single isomers resembles the specificity we

have observed<sup>3,4</sup> in 'chelate-assisted' hydrosilylation at Ir<sup>I</sup> centres and contrasts with the conclusion (based on i.r. and n.m.r. measurements<sup>13</sup>) that the non-chelated silyl ruthenium analogue [Ru(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>] exists in solution as a mixture of three isomeric octahedral components.

The chemistry of complexes of the type (3)–(8) was explored further using the first of these, [Ru(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-SiMe<sub>2</sub>)<sub>2</sub>(CO)<sub>2</sub>], as an example. The marked decrease in  $\nu(\text{CO})$  stretching energy between all-*trans* [Ru(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>Cl<sub>2</sub>] and compound (3) which has been referred to above led us to expect a corresponding increase in difficulty with which CO could be displaced from the metal centre; indeed the silyl complex proves to be extraordinarily inert. While the complexes investigated by Mawby<sup>8</sup> were subject to carbonyl replacement under extremely mild conditions using a variety of neutral substrates, including ethylene, (3) was unaffected by the latter, or by PPh<sub>3</sub> or P(OMe)<sub>3</sub>, with thermal or photochemical activation or following treatment with trimethylamine *N*-oxide. Attempted nucleophilic (Li[BEt<sub>3</sub>H]) or electrophilic (AlCl<sub>3</sub>-PPh<sub>3</sub>) attack at C or O respectively of the co-ordinated carbonyl group and electrophilic addition to Ru (using HBF<sub>4</sub>)

**Table 4.** Important bond distances (Å) and angles (°) for compound (4)

Os(1)–C(1)	1.87(1)	Os(1)–P(2)	2.392(3)	Os(2)–C(3)	1.85(1)	Os(2)–P(4)	2.392(3)
Os(1)–C(2)	1.89(1)	Os(1)–Si(1)	2.472(4)	Os(2)–C(4)	1.88(1)	Os(2)–Si(3)	2.479(4)
Os(1)–P(1)	2.379(3)	Os(1)–Si(2)	2.471(4)	Os(2)–P(3)	2.372(4)	Os(2)–Si(4)	2.485(4)
C(1)–Os(1)–C(2)	160.2(6)	P(1)–Os(1)–Si(1)	82.3(1)	C(3)–Os(2)–C(4)	161.2(6)	P(3)–Os(2)–Si(3)	82.1(1)
C(1)–Os(1)–P(1)	95.1(5)	P(1)–Os(1)–P(2)	102.8(1)	C(3)–Os(2)–P(3)	103.8(4)	P(3)–Os(2)–P(4)	101.6(1)
C(1)–Os(1)–Si(1)	82.9(5)	P(1)–Os(1)–Si(2)	174.4(1)	C(3)–Os(2)–Si(3)	83.7(4)	P(3)–Os(2)–Si(4)	173.7(1)
C(1)–Os(1)–P(2)	96.1(5)	Si(1)–Os(1)–P(2)	174.9(1)	C(3)–Os(2)–P(4)	94.8(4)	Si(3)–Os(2)–P(4)	176.2(1)
C(1)–Os(1)–Si(2)	84.5(5)	Si(1)–Os(1)–Si(2)	92.1(1)	C(3)–Os(2)–Si(4)	80.1(4)	Si(3)–Os(2)–Si(4)	93.5(1)
C(2)–Os(1)–P(1)	97.7(4)	P(2)–Os(1)–Si(2)	82.8(1)	C(4)–Os(2)–P(3)	88.7(4)	P(4)–Os(2)–Si(4)	82.8(1)
C(2)–Os(1)–Si(1)	83.8(4)	Os(1)–C(1)–O(1)	173.0(1)	C(4)–Os(2)–Si(3)	84.3(5)	Os(2)–C(3)–O(3)	174.0(1)
C(2)–Os(1)–P(2)	95.8(4)	Os(1)–C(2)–O(2)	176.0(1)	C(4)–Os(2)–P(4)	96.3(4)	Os(2)–C(4)–O(4)	175.0(1)
C(2)–Os(1)–Si(2)	81.4(4)			C(4)–Os(2)–Si(4)	86.3(5)		

**Figure 2.** ORTEP plots of the two different molecules of compound (4), showing (a) the skew relationship between the chelate ligand backbones around Os(1) (molecule 1), contrasting with (b) the parallel arrangement centred on Os(2) (molecule 2)

likewise led only to recovery of unchanged (3). Oxidative displacement of Si from Ru was observed, however, with boiling  $\text{CCl}_4$ , HCl gas, or  $\text{I}_2$ .

After refluxing for 4 h in  $\text{CCl}_4$ , the initially colourless solution of (3) slowly changed to yellow and a compound (9) was isolated. This product showed two strong  $\nu(\text{CO})$  bands in the i.r. indicating a *cis*-dicarbonyl arrangement and a singlet  $^{31}\text{P}$  n.m.r. signal; while not unambiguous these data suggest the geometry shown since the frequency of  $\nu(\text{CO})$  is indicative of CO *trans* to P rather than Cl. Prolonged treatment of (3) in hot methylene chloride with HCl gas afforded an identical product, while reflux in thf solution with iodine yielded a compound with very similar spectroscopic characteristics which is therefore identified as the iodo analogue, (10), of compound (9). It may be significant in relation to the arguments developed above that release of the silyl functions from the Ru centre is accompanied by a marked shift of  $\nu(\text{CO})$  to higher energy although this could simply be an effect of stereochemical reorganization to give a *cis*-dicarbonyl geometry.

**X-Ray Crystal and Molecular Structure of Compound (4).**—The stereochemistry inferred from the spectroscopic data (Table 1) is confirmed with the chelating silyl units occupying an equatorial plane about the metal centre, *cis* to one another. The molecular geometry for the osmium complex thus closely resembles that established<sup>2</sup> for  $[\text{Pt}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)_2]$ , with CO ligands attached in the axial positions to complete the octahedral  $\text{M}^{\text{II}}$  configuration. An important further feature of

interest in the crystal, however, is the coexistence in the asymmetric unit of two structurally distinct molecules which differ in the relative conformations of the chelate methylene backbones: in one of these the ethylene bridges are parallel to one another while in the other they are skew. This distinction is clear in Figure 2. The arrangement centred on Os(1) renders the chelate C–C bonds skew (*i.e.* antiparallel), corresponding to  $C_2$  molecular symmetry while Os(2) is co-ordinated with the two chelates disposed in a manner similar to that found<sup>2</sup> for  $[\text{Pt}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)_2]$  ( $C_s$  symmetry) where the silyl methyl groups approach an eclipsed relationship with one another.

The two molecules in (4) are specifically differentiated by the dihedral angles, *i.e.* P(1)–Et(1)–Et(2)–Si(1) 57°, P(2)–Et(3)–Et(4)–Si(2) 55° (molecule 1); P(3)–Et(5)–Et(6)–Si(3) –53°, P(4)–Et(7)–Et(8)–Si(4) 54° (molecule 2). The differences between the two geometries closely resemble those found in crystalline ethylenediamine (en) complexes: for example,<sup>14</sup> *trans*- $[\text{PtCl}_2(\text{en})_2]$  adopts a skew configuration while the diamine ligands lie parallel in crystals of *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ . Related skew and parallel geometries have been characterized separately in bis(dppe) complexes in which coplanar co-ordination by the two chelating diphosphines occurs about the metal centre {*e.g.*  $[\text{Mo}(\text{CO})(\text{N}_2)(\text{dppe})_2]\cdot 0.5\text{C}_6\text{H}_6$ <sup>15</sup> and  $[\text{Rh}(\text{dppe})_2]^+^{16}$ }, but so far as we are aware the coexistence of two such conformers in a single crystal has not been observed previously.

The energy difference between these two structures

(molecules 1 and 2) is clearly small with rapid interconversion resulting in average n.m.r. spectra (Table 1) in solution, but differences in site symmetry between distinguishable molecules in the microcrystalline material must account for the splitting of  $\nu(\text{CO})$  bands observed in solid samples. The presence of both conformers in the same crystal suggests a solid-state arrangement imposed by packing effects; by contrast it has been argued previously that conformational flexibility in dppe complexes leads to geometries determined by intramolecular interactions rather than by crystal-packing forces.<sup>16</sup>

The first report of an Os–Si bond appeared only recently, that of 2.410 Å in the triosmium complex  $[\text{Os}_3(\text{CO})_9(\text{SiMeCl}_2)_3(\mu\text{-H})_3]$  which coincidentally also exists as two conformers in the crystallographic unit cell although in a totally different sense (rotamers with opposing orientation of the three silyl groups).<sup>17</sup> The substantially longer Os–Si bond length of 2.477 Å (mean) observed in complex (4) lends additional support to the suggestion<sup>17</sup> that the distance in the silyl osmium trimer is influenced by an increase in  $\pi$ -acceptor strength of  $-\text{SiMeCl}_2$  compared with  $-\text{SiR}_3$ . The M–P distances are also longer than those in the related square-planar  $[\text{Pt}(\text{PPh}_2\text{CH}_2\text{CH}_2\text{SiMe}_2)_2]$  compound;<sup>2</sup> indeed Os–P at 2.385 Å (mean) is much longer than that (2.325 Å) *trans* to H in  $[\text{OsH}(\text{dppe})_2(\text{C}_{10}\text{H}_7)]$  ( $\text{C}_{10}\text{H}_7 = \text{naphthyl}$ ),<sup>18</sup> stressing the exceptional character of the silyl group as a *trans*-influencing ligand.<sup>2–4</sup> By contrast the Os–C distances (mean 1.87 Å) are conspicuously short with the C–O distances (mean 1.19 Å) correspondingly long,<sup>15</sup> consistent with an unusual degree of back-donation from a metal centre which, as we have suggested above, may be electron rich through electron release from Si. Interestingly, the bond angles at the Os atom deviate markedly from regular octahedral geometry: those in the equatorial plane are almost identical with those in the related Pt complex,<sup>2</sup> the Si–M–Si angles being *ca.* 10° less than P–M–P, while the C–Os–C angles depart considerably from linearity (mean 160.6°) and in either conformer the M–C–O linkage is also bent (range 160–177°). These distortions, which can be clearly seen in the Figures, take the CO ligands between the  $\text{SiMe}_2$  termini of the chelates and away from the  $\text{PPh}_2$  groups. It is tempting to dismiss the irregularity as merely reflecting unequal steric demands of the pairs of  $\text{SiMe}_2$  and  $\text{PPh}_2$  groups;<sup>2</sup> however a similar effect observed in *cis*- $[\text{Fe}(\text{CO})_4(\text{SiMe}_3)_2]$ , in which  $\text{C}_{ax}\text{-Fe-C}_{ax}$  is reduced to only 141.3°, is consistent with octahedral deformation towards a bicapped tetrahedral geometry attributable to the electronic influence of strong  $\sigma$ -donor ligands in equatorial sites.<sup>10,19</sup>

## Acknowledgements

We thank the N.S.E.R.C., Canada for the provision of Operating Grants (to S. R. S. and T. S. C.).

## References

- 1 Part 6, M. J. Auburn, S. L. Grundy, S. R. Stobart, and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1985, **107**, 266.
- 2 R. D. Holmes-Smith, S. R. Stobart, T. S. Cameron, and K. Jochem, *J. Chem. Soc., Chem. Commun.*, 1981, 937.
- 3 M. J. Auburn, R. D. Holmes-Smith, and S. R. Stobart, *J. Am. Chem. Soc.*, 1984, **106**, 1314.
- 4 M. J. Auburn and S. R. Stobart, *Inorg. Chem.*, 1985, **24**, 318.
- 5 R. D. Holmes-Smith, R. D. Osei, and S. R. Stobart, *J. Chem. Soc., Perkin Trans. 1*, 1983, 861.
- 6 M. J. Auburn, R. D. Holmes-Smith, S. R. Stobart, M. J. Zaworotko, T. S. Cameron, and A. Kumari, *J. Chem. Soc., Chem. Commun.*, 1983, 1523.
- 7 G. M. Sheldrick, SHELX 76 program for crystal structure determination, University of Cambridge, 1976.
- 8 C. F. J. Barnard, J. A. Daniels, and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1976, 961.
- 9 A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1966, 1707; F. R. Hartley, *Chem. Soc. Rev.*, 1973, **2**, 163.
- 10 L. Vancea, M. J. Bennett, C. E. Jones, R. A. Smith, and W. A. G. Graham, *Inorg. Chem.*, 1977, **16**, 897.
- 11 (a) P. F. Crossing and M. R. Snow, *J. Chem. Soc. A*, 1971, 610; (b) M. Freni, D. Guisto, and P. Romiti, *J. Inorg. Nucl. Chem.*, 1967, **29**, 761.
- 12 R. D. Holmes-Smith, S. R. Stobart, T. S. Cameron, and K. Jochem, unpublished work.
- 13 S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 1969, 2559.
- 14 C. F. Liu and J. A. Ibers, *Inorg. Chem.*, 1970, **9**, 773; A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, 1952, **25**, 331.
- 15 M. Sato, T. Tatsumi, T. Kodama, M. Hidai, T. Uchida, and Y. Uchida, *J. Am. Chem. Soc.*, 1978, **100**, 4447.
- 16 M. C. Hall, B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc. A*, 1970, 2539.
- 17 G. N. van Buuren, A. C. Willis, F. W. B. Einstein, L. K. Peterson, R. K. Pomeroy, and D. Sutton, *Inorg. Chem.*, 1981, **20**, 4361.
- 18 U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1971, 1118.
- 19 R. Hoffmann, J. M. Howell, and A. R. Rossi, *J. Am. Chem. Soc.*, 1976, **98**, 2484.

Received 10th February 1986; Paper 6/287