

its counterpart in  $\text{PF}_5$ <sup>14</sup> ( $r(\text{P}-\text{F}_a) = 1.577 \text{ \AA}$ ,  $r(\text{P}-\text{F}_e) = 1.534 \text{ \AA}$ ). At the same time the sum of the bond orders of the phosphorus bonds, estimated from Pauling's empirical bond order-bond length formula using the Schomaker-Stevenson radii with correction for electronegativity difference,<sup>17</sup> decreases from 7.2 ( $\text{PF}_5$ ) through 6.1 ( $\text{PCl}_2\text{F}_3$ ) to 4.6 ( $\text{PCl}_5$ ). The decrease in bond order may be attributed to a parallel decreasing participation of phosphorus 3d orbitals in the bonding from that atom: as the fluorine atoms in  $\text{PF}_5$  are replaced by the less electronegative chlorines, the positive charge on phosphorus decreases, the 3p-3d energy gap increases, and the bonding contribution of the 3d orbitals becomes smaller. One may suppose that, in the limit of no 3d participation, the equatorial bonds are  $\text{sp}^2$  hybrids and the axial bonds are three-center bonds involving the last phosphorus p orbital. The more rapid increase in the axial compared to the equatorial bond lengths as fluorine atoms are replaced, for example in the series  $\text{PF}_5 \rightarrow \text{PCl}_2\text{F}_3 \rightarrow \text{PCl}_5$ , is consistent with this picture.

It is by now well established, especially from NMR experiments,<sup>5,6</sup> that the equatorial and axial fluorine atoms in pentavalent phosphorus compounds undergo rapid exchange at ordinary temperatures. It has also been shown<sup>18</sup> that the mechanism for the exchange is almost certainly the Berry inversion.<sup>2</sup> Since the

Berry mechanism leads to at least one chlorine atom in an axial site in the case of  $\text{PCl}_2\text{F}_3$ , it was hoped that our measurements would provide direct structural evidence for the consequences of Berry inversion. Unfortunately, the results in Table II indicate that we have no proof of the presence of  $\text{PCl}_a\text{Cl}_e\text{F}_3$  in our sample: the allowance for possible  $\text{PF}_3\text{O}$  (model A compared to model B) leads to significantly better agreement than does allowance for  $\text{PCl}_a\text{Cl}_e\text{F}_3$  (model B compared to model C). Similar remarks could, of course, be made about the isomer  $\text{P}(\text{Cl}_a)_2\text{F}_3$ . Nevertheless, if one regards the value 0.056 as an upper limit for the mole fraction of  $\text{PCl}_a\text{Cl}_e\text{F}_3$  (model B), one may make a crude estimate of the lower limit for the free energy difference of the two isomers. The result for  $\Delta G^\circ = G^\circ(\text{PCl}_a\text{Cl}_e\text{F}_3) - G^\circ(\text{P}(\text{Cl}_a)_2\text{F}_3)$  calculated from the mole ratio 0.056/0.94 is about 1.7 kcal/mol at room temperature and is consistent with the value  $7.2 \pm 0.5$  kcal/mol estimated<sup>5a</sup> for the activation energy of the interconversion.

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**Registry No.**  $\text{PCl}_2\text{F}_3$ , 13454-99-4.

**Supplementary Material Available:** Tables of total scattered intensities, calculated backgrounds, and average molecular intensities from two camera distances (9 pages). Ordering information is given on any current masthead page.

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## Axial-Equatorial Isomerism in the Complexes $\text{M}(\text{CO})_4(\text{L})$ ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ; $\text{L} = \text{Group } 15^\dagger \text{ Ligand}$ ). Crystal Structures of $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$ , $\text{ax-Ru}(\text{CO})_4(\text{SbMe}_3)$ , and $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$

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The compounds  $\text{M}(\text{CO})_4(\text{L})$  ( $\text{M} = \text{Fe}, \text{Ru}, \text{Os}$ ;  $\text{L} = \text{EPh}_3$ ,  $\text{E} = \text{P}, \text{As}, \text{Sb}$ ;  $\text{L} = \text{PMe}_3$ ,  $\text{P}(\text{OCH}_2)_3\text{CMe}$ .  $\text{M} = \text{Ru}, \text{Os}$ ;  $\text{L} = \text{SbMe}_3$ ) have been synthesized from  $\text{L}$  and  $\text{M}(\text{CO})_5$ . The crystal structures of  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$ ,  $\text{ax-Ru}(\text{CO})_4(\text{SbMe}_3)$ , and  $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$  have been determined by X-ray crystallography.  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$ : space group  $\text{P}\bar{1}$ ;  $a = 10.605$  (3),  $b = 11.068$  (4),  $c = 9.979$  (3)  $\text{\AA}$ ;  $\alpha = 113.57$  (3),  $\beta = 93.14$  (3),  $\gamma = 91.47$  (3) $^\circ$ ;  $Z = 2$ ;  $R_1 = 0.020$ ,  $R_2 = 0.021$  (1650 observed reflections);  $\text{AsPh}_3$  in an axial position of the trigonal-bipyramidal coordination sphere,  $\text{Ru-As} = 2.461$  (1)  $\text{\AA}$ .  $\text{ax-Ru}(\text{CO})_4(\text{SbMe}_3)$ : space group  $R\bar{3}$ ,  $a = 10.378$  (1),  $c = 9.632$  (1)  $\text{\AA}$ ;  $Z = 3$ ;  $R_1 = 0.023$ ,  $R_2 = 0.030$  (523 observed reflections);  $\text{SbMe}_3$  axial,  $\text{Ru-Sb} = 2.619$  (1)  $\text{\AA}$ .  $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$ : space group  $\text{P}\bar{1}$ ;  $a = 11.123$  (2),  $b = 11.284$  (4),  $c = 12.714$  (4)  $\text{\AA}$ ;  $\alpha = 129.29$  (2),  $\beta = 102.35$  (2),  $\gamma = 102.45$  (2) $^\circ$ ;  $Z = 2$ ;  $R_1 = 0.019$ ,  $R_2 = 0.021$  (3115 observed reflections);  $\text{SbPh}_3$  equatorial,  $\text{Os-Sb} = 2.612$  (2)  $\text{\AA}$ . Infrared spectroscopy revealed that in solution many of the complexes exhibited axial-equatorial isomerism. The tendency to give the less common equatorial isomer was  $\text{Ru} > \text{Os} \gg \text{Fe}$ ,  $\text{Sb} > \text{As} > \text{P}$ ,  $\text{Ph} > \text{Me}$ , and  $\text{P}(\text{OCH}_2)_3\text{CMe} > \text{PMe}_3$ ,  $\text{PPh}_3$ . The order for the group 15 element was rationalized in terms of the  $\sigma$ -donor ability of the element: in agreement with theoretical predictions, weaker donors prefer the equatorial site. The  $\pi$ -bonding ability of the ligands may also be important in determining the other trends. Carbon-13 NMR spectra, which revealed the isomers were in rapid equilibrium in solution, were also recorded.

### Introduction

The site preference of ligands in trigonal-bipyramidal complexes has been the subject of considerable theoretical and experimental interest.<sup>1-9</sup> For most compounds of the type  $\text{M}(\text{CO})_4(\text{L})$  ( $\text{M} = \text{Fe}, \text{Ru}$ ;  $\text{L} = \text{group } 15 \text{ ligand}$ ), spectroscopic and crystallographic evidence shows that the non-carbonyl ligand adopts an axial site in the coordination sphere of the metal.<sup>5,10-14</sup> This site preference has usually been rationalized in terms of the  $\pi$ -acceptor properties

of the ligands: the better  $\pi$ -acceptor ligand, CO, has a greater preference for the equatorial position.<sup>15</sup> This assumption has

<sup>†</sup> In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III  $\rightarrow$  3 and 13.)

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**Table I.** Analytical and Mass Spectral Data for New  $M(\text{CO})_4(\text{L})$  Derivatives

compd	% calcd		% found		mass spectrum <sup>a</sup>
	C	H	C	H	
$\text{Ru}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CMe}]$	29.92	2.51	29.95	2.50	362 (P <sup>+</sup> )
$\text{Ru}(\text{CO})_4(\text{PMe}_3)$	29.07	3.14	29.01	3.16	290 (P <sup>+</sup> )
$\text{Ru}(\text{CO})_4(\text{AsPh}_3)$	50.89	2.91	50.92	2.89	dec
$\text{Ru}(\text{CO})_4(\text{SbMe}_3)$	22.13	2.39	22.19	2.19	382 (P <sup>+</sup> )
$\text{Os}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CMe}]$	24.15	2.01	23.99	1.90	452 (P <sup>+</sup> )
$\text{Os}(\text{CO})_4(\text{PMe}_3)$	22.22	2.40	22.25	2.40	380 (P <sup>+</sup> )
$\text{Os}(\text{CO})_4(\text{AsPh}_3)$	43.43	2.48	43.51	2.57	610 (P <sup>+</sup> )
$\text{Os}(\text{CO})_4(\text{SbMe}_3)$	17.91	1.92	17.89	1.93	470 (P <sup>+</sup> )
$\text{Os}(\text{CO})_4(\text{SbPh}_3)$	40.32	2.31	40.43	2.58	656 (P <sup>+</sup> )

<sup>a</sup> Most intense peak of parent ion envelope; in all cases the parent ion agreed with that simulated by computer.

received support in the theoretical study of five-coordination of Rossi and Hoffmann.<sup>1</sup> That the solid-state structure of  $\text{Mn}(\text{C}-\text{O})_4(\text{NO})$  revealed the NO group in an equatorial site,<sup>16</sup> and that  $\text{M}(\text{CO})_4(\text{PF}_3)$  ( $\text{M} = \text{Fe}, \text{Ru}$ )<sup>17</sup> existed in solution as a mixture of axial and equatorial isomers, was consistent with the known good  $\pi$ -acceptor properties of the NO and  $\text{PF}_3$  ligands. Similar arguments may also be employed to explain why when L is an alkene it is invariably found in the equatorial site.<sup>1,8,18</sup>

The crystal structure of  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  was then of special interest since it showed that the group 15 ligand was equatorial.<sup>19</sup> The solution infrared spectrum was also atypical of an axially substituted  $\text{M}(\text{CO})_4(\text{L})$  molecule, which indicated the anomaly was not just a solid-state effect.<sup>19</sup> Since there is no evidence to suggest that  $\text{SbPh}_3$  is a better  $\pi$  acceptor than CO, the site preference of the antimony ligand cannot be rationalized by using  $\pi$ -bonding arguments.

We have recently reported a convenient preparation of the pentacarbonyls of ruthenium and osmium.<sup>20</sup> The ready availability of these compounds has allowed the preparation of analogues to  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  and the study of the site preference of other group 15 ligands in ruthenium and osmium tetracarbonyl complexes. Herein, we report the details of this study, which show that axial-equatorial isomerism is a feature of the heavier members of these complexes. Furthermore, the occurrence of the less common equatorial isomer is best explained in terms of the  $\sigma$ -donor rather than the  $\pi$ -acceptor properties of the ligands. A preliminary communication of this work has been published.<sup>21</sup>

## Experimental Section

Unless otherwise stated, manipulations of starting materials and products were carried out under a nitrogen atmosphere with use of standard Schlenk techniques. Hexane was refluxed over potassium and THF over potassium benzophenone ketyl; they were distilled and stored under nitrogen before use. The pentacarbonyls of ruthenium and osmium were prepared by a literature method;<sup>20</sup>  $\text{Fe}(\text{CO})_5$  was commercially available. The group 15 ligand  $\text{P}(\text{OCH}_2)_3\text{CMe}$  was synthesized by the method of Heitsch and Verkade;<sup>22</sup> it was sublimed before use. Other ligands were commercially available. The iron complexes  $\text{Fe}(\text{CO})_4(\text{L})$

**Table II.** Crystallographic Data for  $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$ ,  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$ , and  $\text{Ru}(\text{CO})_4(\text{SbMe}_3)$ 

	$\text{Ru}(\text{CO})_4$ - (AsPh <sub>3</sub> )	$\text{Os}(\text{CO})_4$ - (SbPh <sub>3</sub> )	$\text{Ru}(\text{CO})_4$ - (SbMe <sub>3</sub> )
fw	519.4	655.3	380.0
space group	$P\bar{1}$	$P\bar{1}$	$R_3$
cryst syst	triclinic	triclinic	hexagonal
a, Å	10.605 (3)	11.123 (2)	10.378 (1)
b, Å	11.068 (4)	11.284 (4)	
c, Å	9.979 (3)	12.714 (4)	9.632 (1)
$\alpha$ , deg	113.57 (3)	129.29 (2)	90
$\beta$ , deg	93.14 (3)	102.35 (2)	
$\gamma$ , deg	91.47 (3)	102.45 (2)	120
V, Å <sup>3</sup>	1070.6	1068.5	898.3
Z	2	2	3
$d_{\text{calcd}}$ , g/cm <sup>3</sup>	1.611	2.037	2.057
$d_{\text{found}}$ , g/cm <sup>3</sup>	1.50	1.99	2.10
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	22.70	71.81	33.99
cryst size, mm	0.24 × 0.22 × 0.030	0.076 × 0.11 × 0.22	0.61 × 0.37 × 0.14

**Table III.** Diffractometer Collection Data and Refinement Parameters

	$\text{Ru}(\text{CO})_4$ - (AsPh <sub>3</sub> )	$\text{Os}(\text{CO})_4$ - (SbPh <sub>3</sub> )	$\text{Ru}(\text{CO})_4$ - (SbMe <sub>3</sub> )
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data colln range ( $2\theta$ ), deg	3.5–40.0	3.5–45.0	3.0–50.0
scan width ( $2\theta$ ), deg	1.40	1.20	1.3
scan rate ( $2\theta$ ), deg/min	2	2	1.3–6.6
colln range	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, \pm k, \pm l$
transmission coeff range	0.594–0.932	0.365–0.644	0.913–1.000 <sup>a</sup>
no. of unique reflns	2018	3754	582
no. of obsd. reflns ( $I > 2.3\sigma_I$ )	1650	3115	523
no. of variables in final cycle	253	298	39
$R_1^b$	0.0203	0.0192	0.0233
$R_2^c$	0.0213	0.0205	0.0295
GOF	1.0463	1.3989	0.9806
largest nonhydrogen shift/error	0.15	0.36	0.00

<sup>a</sup> Empirical absorption correction; see text. <sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>c</sup>  $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ .

**Table IV.** Fractional Coordinates for  $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$ 

atom	x	y	z
Ru	0.35373 (4)	0.19970 (4)	0.23603 (5)
As	0.20818 (5)	0.31855 (5)	0.13740 (5)
C(1)	0.2193 (5)	0.0705 (5)	0.2070 (6)
C(2)	0.3699 (5)	0.3512 (5)	0.4186 (6)
C(3)	0.4571 (5)	0.1771 (5)	0.0764 (6)
C(4)	0.4686 (5)	0.1122 (5)	0.3134 (6)
O(1)	0.1387 (4)	-0.0043 (4)	0.1941 (5)
O(2)	0.3770 (4)	0.4417 (4)	0.5281 (4)
O(3)	0.5152 (4)	0.1628 (5)	-0.0202 (5)
O(4)	0.5392 (4)	0.0582 (4)	0.3591 (5)
C(11)	0.1925 (4)	0.2555 (5)	-0.0744 (5)
C(12)	0.1768 (5)	0.1237 (6)	-0.1561 (6)
C(13)	0.1618 (6)	0.0733 (6)	-0.3085 (6)
C(14)	0.1657 (6)	0.1601 (8)	-0.3739 (6)
C(15)	0.1809 (6)	0.2903 (7)	-0.2955 (7)
C(16)	0.1940 (5)	0.3399 (6)	-0.1438 (6)
C(21)	0.2510 (4)	0.5048 (5)	0.2005 (5)
C(22)	0.1593 (5)	0.5956 (5)	0.2319 (5)
C(23)	0.1908 (6)	0.7290 (5)	0.2790 (6)
C(24)	0.3150 (7)	0.7693 (6)	0.2932 (7)
C(25)	0.4056 (6)	0.6821 (7)	0.2627 (8)
C(26)	0.3747 (5)	0.5474 (6)	0.2164 (7)
C(31)	0.0355 (4)	0.3147 (4)	0.1864 (5)
C(32)	-0.0632 (5)	0.2969 (6)	0.0869 (6)
C(33)	-0.1869 (5)	0.2937 (7)	0.1231 (7)
C(34)	-0.2120 (5)	0.3095 (6)	0.2592 (7)
C(35)	-0.1163 (6)	0.3277 (7)	0.3604 (6)
C(36)	0.0083 (5)	0.3305 (6)	0.3245 (6)

were prepared by literature methods<sup>23</sup> or with minor variations thereof. The method used previously to prepare  $\text{Ru}(\text{CO})_4[\text{P}(\text{OMe})_3]$  from  $\text{Ru}_3$ -

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Table V. Fractional Coordinates for Os(CO)<sub>4</sub>(SbPh<sub>3</sub>)

atom	x	y	z
Os	0.67903 (2)	0.44175 (3)	0.21107 (2)
Sb	0.82775 (3)	0.69625 (4)	0.50892 (3)
C(1)	0.5342 (6)	0.4872 (8)	0.1543 (7)
C(2)	0.7344 (8)	0.2647 (8)	0.1069 (7)
C(3)	0.5592 (7)	0.3104 (9)	0.2312 (8)
C(4)	0.7885 (6)	0.5495 (7)	0.1677 (6)
O(1)	0.4473 (5)	0.5078 (7)	0.1140 (6)
O(2)	0.7634 (7)	0.1558 (7)	0.0360 (6)
O(3)	0.4920 (6)	0.2333 (9)	0.2420 (8)
O(4)	0.8507 (5)	0.6056 (6)	0.1364 (5)
C(11)	0.7652 (5)	0.8940 (6)	0.6142 (5)
C(12)	0.6238 (6)	0.8461 (8)	0.5595 (6)
C(13)	0.5798 (6)	0.9708 (9)	0.6204 (7)
C(14)	0.6749 (7)	1.1420 (9)	0.7331 (8)
C(15)	0.8158 (6)	1.1920 (7)	0.7904 (7)
C(16)	0.8601 (5)	1.0679 (7)	0.7306 (6)
C(21)	0.8263 (5)	0.6416 (6)	0.6418 (5)
C(22)	0.8276 (7)	0.7558 (7)	0.7808 (6)
C(23)	0.8282 (8)	0.7170 (9)	0.8642 (8)
C(24)	0.8277 (8)	0.5698 (9)	0.8124 (8)
C(25)	0.8271 (8)	0.4556 (9)	0.6753 (8)
C(26)	0.8266 (7)	0.4895 (7)	0.5878 (7)
C(31)	1.0440 (5)	0.8531 (6)	0.6123 (5)
C(32)	1.1363 (5)	0.9006 (7)	0.7390 (6)
C(33)	1.2762 (5)	1.0091 (8)	0.8101 (6)
C(34)	1.3246 (5)	1.0726 (7)	0.7557 (6)
C(35)	1.2343 (6)	1.0236 (8)	0.6285 (7)
C(36)	1.0945 (5)	0.9146 (7)	0.5565 (6)

Table VI. Fractional Coordinates for Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>)

atom	x	y	z
Ru	0	0	0
Sb	0	0	-0.27183 (9)
C(1)	0	0	0.196 (2)
C(2)	-0.206 (1)	-0.052 (1)	-0.0066 (8)
C(3)	-0.176 (1)	-0.194 (1)	-0.3682 (9)
O(1)	0.0	0.0	0.317 (1)
O(2)	-0.326 (8)	-0.080 (1)	-0.0091 (9)

Table VII. Selected Molecular Dimensions for Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>)

(a) Bond Lengths (Å)		
	obsd	cor
Ru-As	2.461 (1)	2.507 <sup>a</sup>
Ru-C(1)	1.918 (5)	1.930 <sup>b</sup>
Ru-C(2)	1.915 (5)	1.921 <sup>b</sup>
Ru-C(3)	1.921 (5)	1.932 <sup>b</sup>
Ru-C(4)	1.890 (5)	1.906 <sup>b</sup>
C(1)-O(1)	1.140 (7)	1.153 <sup>c</sup>
C(2)-O(2)	1.147 (6)	1.160 <sup>c</sup>
C(3)-O(3)	1.132 (7)	1.146 <sup>c</sup>
C(4)-O(4)	1.153 (6)	1.168 <sup>c</sup>
As-C(11)	1.938 (5)	
As-C(21)	1.932 (5)	
As-C(31)	1.925 (5)	
(b) Bond Angles (deg)		
C(1)-Ru-C(2)	117.9 (2)	O(2)-C(2)-Ru 178.6 (4)
C(1)-Ru-C(3)	118.5 (2)	O(3)-C(3)-Ru 178.1 (5)
C(1)-Ru-C(4)	92.5 (2)	O(4)-C(4)-Ru 179.2 (5)
C(2)-Ru-C(3)	123.4 (2)	C(11)-As-C(21) 103.1 (2)
C(2)-Ru-C(4)	90.0 (2)	C(11)-As-C(31) 103.0 (2)
C(3)-Ru-C(4)	91.5 (2)	C(21)-As-C(31) 103.3 (2)
As-Ru-C(1)	89.0 (1)	C(Ph)-As-C(Ph) <sup>d</sup> 103.1
As-Ru-C(2)	89.1 (1)	Ru-As-C(11) 115.4 (1)
As-Ru-C(3)	88.0 (1)	Ru-As-C(21) 115.1 (1)
As-Ru-C(4)	178.5 (2)	Ru-As-C(31) 115.2 (1)
O(1)-C(1)-Ru	177.9 (5)	Ru-As-C(Ph) <sup>d</sup> 115.2
(c) Torsion Angles (deg)		
C(11)-As-Ru-C(3)	34.24	C(31)-As-Ru-C(1) 35.57
C(21)-As-Ru-C(2)	37.67	

<sup>a</sup> Atoms assumed to move independently. <sup>b</sup> Second atom named assumed to ride on the first atom. <sup>c</sup> Both atoms assumed to ride on Ru. <sup>d</sup> Mean value.

Table VIII. Selected Molecular Dimensions for Os(CO)<sub>4</sub>(SbPh<sub>3</sub>)

(a) Bond Lengths (Å)			
	obsd	cor	
Os-Sb	2.612 (2)	2.649 <sup>a</sup>	
Os-C(1)	1.926 (6)	1.934 <sup>b</sup>	
Os-C(2)	1.911 (7)	1.933 <sup>b</sup>	
Os-C(3)	1.952 (6)	1.980 <sup>b</sup>	
Os-C(4)	1.939 (6)	1.945 <sup>b</sup>	
C(1)-O(1)	1.134 (7)	1.148 <sup>c</sup>	
C(2)-O(2)	1.148 (8)	1.164 <sup>c</sup>	
C(3)-O(3)	1.117 (8)	1.138 <sup>c</sup>	
C(4)-O(4)	1.134 (7)	1.150 <sup>c</sup>	
Sb-C(11)	2.131 (5)		
Sb-C(21)	2.136 (5)		
Sb-C(31)	2.124 (5)		
(b) Bond Angles (deg)			
C(1)-Os-C(2)	136.4 (3)	O(2)-C(2)-Os	175.6 (6)
C(1)-Os-C(3)	90.7 (3)	O(3)-C(3)-Os	178.6 (8)
C(1)-Os-C(4)	88.8 (2)	O(4)-C(4)-Os	177.1 (5)
C(2)-Os-C(3)	88.6 (3)	C(11)-Sb-Os	114.0 (1)
C(2)-Os-C(4)	87.6 (3)	C(21)-Sb-Os	118.4 (1)
C(3)-Os-C(4)	173.8 (3)	C(31)-Sb-Os	121.2 (1)
Sb-Os-C(1)	107.0 (2)	C(Ph)-Sb-Os <sup>d</sup>	117.9
Sb-Os-C(2)	116.6 (2)	C(11)-Sb-C(21)	100.1 (2)
Sb-Os-C(3)	90.7 (2)	C(11)-Sb-C(31)	99.0 (2)
Sb-Os-C(4)	95.4 (2)	C(21)-Sb-C(31)	100.5 (2)
O(1)-C(1)-Os	176.9 (5)	C(Ph)-Sb-C(Ph) <sup>d</sup>	99.9
(c) Torsion Angles (deg)			
C(21)-Sb-Os-C(3)	22.97	C(31)-Sb-Os-C(4)	31.03

<sup>a</sup> Atoms assumed to move independently. <sup>b</sup> Second atom named assumed to ride on first atom. <sup>c</sup> Both atoms assumed to ride on Os. <sup>d</sup> Mean value.

Table IX. Selected Molecular Dimensions for Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>)

(a) Bond Lengths (Å)		
	obsd	cor
Ru-Sb	2.6187 (9)	2.6578 <sup>a</sup>
Ru-C(1)	1.89 (2)	1.90 <sup>b</sup>
Ru-C(2)	1.92 (1)	1.94 <sup>b</sup>
Sb-C(3)	2.140 (7)	
C(1)-O(1)	1.16 (2)	1.17 <sup>c</sup>
C(2)-O(2)	1.13 (1)	1.15 <sup>c</sup>
(b) Bond Angles		
C(1)-Ru-C(2)	91.9 (2)	Ru-Sb-C(3) 115.7 (2)
C(2)-Ru-C(2)	119.89 (3)	C(3)-Sb-C(3) 102.6 (3)
Ru-Sb-C(1)	180	Ru-C(2)-O(2) 178.3 (9)

<sup>a</sup> Atoms assumed to move independently. <sup>b</sup> Second atom assumed to ride first. <sup>c</sup> Both atoms assumed to ride on Ru.

(CO)<sub>12</sub> was used for Ru(CO)<sub>4</sub>(PMe<sub>3</sub>)<sub>4</sub>.<sup>14</sup> Reactions under moderate CO pressure were carried out in a 200-mL general-purpose bomb from Parr Instrument Co.

Infrared spectra were obtained with a Perkin-Elmer 983 spectrometer, NMR spectra with a Burker 400-MHz instrument, and mass spectra with a Hewlett Packard 5985 GC-MS system with an ionization voltage of 70 eV. Microanalyses were performed by M. K. Yang of the Microanalytical Laboratory of Simon Fraser University. Analytical and mass spectral data for new compounds are given in Table I; infrared and <sup>13</sup>C NMR spectroscopic results in Table X.

**Caution!** In view of the known toxic properties of Fe(CO)<sub>5</sub> care should be taken when handling Ru(CO)<sub>5</sub> and Os(CO)<sub>5</sub>. Also the ligands Me<sub>3</sub>P and Me<sub>3</sub>Sb ignite spontaneously in air.

Because of the nature of the preparations of Ru(CO)<sub>5</sub> and Os(CO)<sub>5</sub>, the concentrations of the hexane solutions of these compounds could only be determined approximately. For most preparations described below the concentration of Ru(CO)<sub>5</sub> in hexane was  $\approx 2 \times 10^{-2}$  M; for Os(CO)<sub>5</sub> it was  $\approx 7 \times 10^{-3}$  M.

**Preparation of Ru(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe].** A solution of Ru(CO)<sub>5</sub> in hexane and a slight excess of P(OCH<sub>2</sub>)<sub>3</sub>CMe was stirred in the dark at

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**Table X.** Infrared and  $^{13}\text{C}$  NMR Data for  $\text{M}(\text{CO})_4(\text{L})$  Compounds

compd	$\nu(\text{CO}),^a \text{cm}^{-1}$						$^{13}\text{C}$ NMR, <sup>b</sup> ppm
	eq	ax	eq	ax	eq	ax	
$\text{Fe}(\text{CO})_4(\text{PMe}_3)$		2051		1978		1937	214.2 (20.8)
$\text{Fe}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CMe}]$		2070		1997		1970	212.2 (25.5)
$\text{Fe}(\text{CO})_4(\text{PPh}_3)$		2052		1979		1947	209.0 (18.7)
$\text{Fe}(\text{CO})_4(\text{AsPh}_3)$		2051		1977		1947	213.7
$\text{Fe}(\text{CO})_4(\text{SbPh}_3)$		2048		1976		1946	212.7
$\text{Ru}(\text{CO})_4(\text{PMe}_3)$		2061		1985		1947	205.3 (2.4)
$\text{Ru}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CMe}]$	2093	2076	2014	2006		1976	203.3 (10.5)
$\text{Ru}(\text{CO})_4(\text{PPh}_3)$		2062		1988		1955	204.6 (3.5)
$\text{Ru}(\text{CO})_4(\text{AsPh}_3)$	2079	2061	1999	1986		1958	204.7
$\text{Ru}(\text{CO})_4(\text{SbMe}_3)$	2071	2060	1988	1988	1965	1952	203.4
$\text{Ru}(\text{CO})_4(\text{SbPh}_3)$	2078	2060	1999	1987	1967		207.4
$\text{Os}(\text{CO})_4(\text{PMe}_3)$		2061		1980		1939	189.9 (4.5)
$\text{Os}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CMe}]$	2092	2076	2009	2001		1967	186.7 (12.5)
$\text{Os}(\text{CO})_4(\text{PPh}_3)$		2061		1983		1946	189.4 (6.0)
$\text{Os}(\text{CO})_4(\text{AsPh}_3)$	2077	2061	1991	1981		1947	188.7
$\text{Os}(\text{CO})_4(\text{SbMe}_3)$	2069	2058		1977	1955	1942	188.2
$\text{Os}(\text{CO})_4(\text{SbPh}_3)$	2076	2060	1992	1978	1957	1950	190.1

<sup>a</sup> All spectra recorded in hexane. <sup>b</sup> Spectra recorded at room temperature in  $\text{CD}_2\text{Cl}_2$ - $\text{CH}_2\text{Cl}_2$  (1:5) or  $\text{CD}_2\text{Cl}_2$  solution;  $J_{\text{PC}}$  (Hz) in parentheses.

room temperature for 18 h during which a pale yellow precipitate formed. The mother solution was then removed and the precipitate washed with hexane ( $3 \times 5 \text{ mL}$ ). The precipitate was recrystallized from a large volume of lukewarm hexane to give the product as pale yellow needles (yield  $\approx 50\%$ ).

**Preparation of  $\text{Ru}(\text{CO})_4(\text{EPh}_3)$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ).** A hexane solution of  $\text{Ru}(\text{CO})_5$  and an approximate twofold molar excess of the ligand were stirred under CO pressure (ca. 25 atm) at room temperature for 18 h. After this period the gas was released and the solvent removed on the vacuum line to leave a yellow-orange powder. Recrystallization of the powder twice from hexane gave the pure  $\text{Ru}(\text{CO})_4(\text{EPh}_3)$  product in  $\approx 35\%$  yield. The arsenic derivative was thermally unstable and slowly decomposed when stored at room temperature. The preparation of  $\text{Ru}(\text{CO})_4(\text{PPh}_3)$  from  $\text{Ru}(\text{CO})_5$  and  $\text{PPh}_3$  has been reported previously.<sup>24</sup>

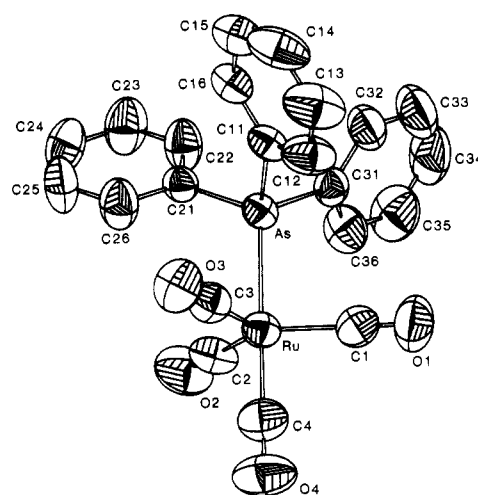
**Preparation of  $\text{Ru}(\text{CO})_4(\text{SbMe}_3)$ .** A solution of  $\text{Ru}(\text{CO})_5$  in hexane (20 mL) was placed in a Carius tube. The tube was cooled to  $-196^\circ\text{C}$  and evacuated; the solution was degassed with one freeze-thaw cycle. With the vessel at room temperature an approximate equimolar quantity of  $\text{SbMe}_3$  was added and the tube pressurized with CO (2 atm). The solution was then stirred in the dark at room temperature for 5 h. After this period the gases were released, and the solution was transferred to a Schlenk tube and evaporated to dryness at  $0^\circ\text{C}$ . The pure, pale yellow product was obtained by sublimation (static atmosphere,  $<0.02 \text{ mm}$ ) onto a probe cooled with cold water; the yield was about 40%.

**Preparation of  $\text{Os}(\text{CO})_4(\text{PMe}_3)$ . Method 1.** The compound was prepared in excellent yield by the reaction of equimolar quantities of  $\text{PMe}_3$  and  $\text{Os}(\text{CO})_5$  in hexane at  $120^\circ\text{C}$  under CO pressure (40 atm) for 16 h. The white compound was purified by sublimation at  $35^\circ\text{C}$  ( $<0.02 \text{ mm}$ , static vacuum), to a probe at  $-78^\circ\text{C}$ .

**Method 2.** This derivative was also prepared (in excellent yield) by heating  $\text{Os}_3(\text{CO})_{12}$  and  $\text{PMe}_3$  (1:3 molar ratio) in hexane at  $280^\circ\text{C}$  under CO (200 atm) for 48 h. The compound was isolated as in Method 1.

**Preparation of  $\text{Os}(\text{CO})_4(\text{SbMe}_3)$ .** Approximately equimolar quantities of  $\text{Os}(\text{CO})_5$  and  $\text{SbMe}_3$  in hexane were heated at  $80^\circ\text{C}$  under CO (33 atm) for 16 h. After the reaction vessel was cooled and the CO released, the solution was transferred to a Schlenk tube and evaporated to dryness on the vacuum line. The pure, pale yellow  $\text{Os}(\text{CO})_4(\text{SbMe}_3)$  (11% yield) was isolated by sublimation from the residue (static vacuum,  $<0.02 \text{ mm}$ , cold-water probe).

**Preparation of  $\text{Os}(\text{CO})_4(\text{EPh}_3)$  ( $\text{E} = \text{As}, \text{Sb}$ ).** Approximately equimolar quantities of  $\text{Os}(\text{CO})_5$  and  $\text{EPh}_3$  in hexane were heated at  $90^\circ\text{C}$  under CO (25 atm). The resulting solution was evacuated to dryness, which also served to remove unreacted  $\text{Os}(\text{CO})_5$ . The remaining solid was dissolved in a minimum of hexane and chromatographed on silica gel (column  $20 \times 2.5 \text{ cm}$ ), with an eluant of hexane-THF (11:1). (Although occasional exposure of the solutions to air appeared not to affect the chromatography, the other conditions were found to be critical to the successful separation of the desired product.) During the chromatography three bands formed, the first two were yellow, and the third very pale yellow to almost colorless. The first ( $\text{Os}_3(\text{CO})_{12}$ ) and third (probably  $\text{Os}_3(\text{CO})_{11}(\text{EPh}_3)$ ) bands were discarded. The second band yielded the product,  $\text{Os}(\text{CO})_4(\text{EPh}_3)$ , which was recrystallized from

**Figure 1.** ORTEP diagram of  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$ .

hexane to give pale yellow crystals (15% yield). The triphenylphosphine analogue,  $\text{Os}(\text{CO})_4(\text{PPh}_3)$ ,<sup>24</sup> was prepared similarly, in much better yield.

**X-ray Crystallography.  $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$  and  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$ .** Details are given here for the crystallographic analysis of  $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$  with differences for  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$  noted in parentheses unless otherwise stated.

Pale yellow platelike crystals suitable for X-ray analysis were grown from hexane. Oscillation, Weissenberg, and precession photographs were taken with  $\text{Cu K}\alpha$  radiation. These allowed the space group  $P\bar{1}$  or  $P1$  and approximate cell dimensions to be assigned. The space group was subsequently determined as  $P\bar{1}$  during structure solution. Accurate cell dimensions were determined by a least-squares refinement of 24 (22) reflections in the range  $2\theta = 16.2$ - $25.4^\circ$  ( $30.9$ - $42.4^\circ$ ) on a Picker FACS-I four circle automated diffractometer that employed graphite-monochromated  $\text{Mo K}\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$  at  $20 \pm 1^\circ\text{C}$ .

Details of the data collection are given in Table II, other crystallographic data in Table III. Stationary-crystal stationary-counter background counts of 10% of the scan time were taken at each side of the scan. Peak-profile analysis<sup>25</sup> was performed on all reflections to derive the intensity,  $I$ , and the associated error,  $\sigma(I)$ . Two standards were measured after every 70 reflections; they gave no indication of decomposition. The data were corrected for Lorentz and polarization effects, and an analytic absorption correction<sup>26</sup> was also applied.

The structures were solved by conventional Patterson and Fourier methods. All non-hydrogen atoms were located by successive difference maps. The final refinement was by block-diagonal least-squares methods with anisotropic parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated (or previously refined) positions. Unit weights were used throughout for both structures. There were no sig-

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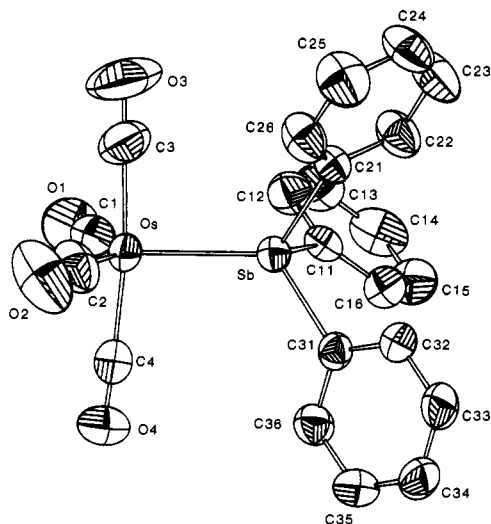


Figure 2. ORTEP diagram of eq-Os(CO)<sub>4</sub>(SbPh<sub>3</sub>).

nificant trends in the average  $\sum w|F_o - F_c|^2$  as a function of  $|F_o|$  and  $(\sin \theta)/\lambda$  in the final error analysis. Atomic scattering factors including anomalous dispersion for non-hydrogen atoms were taken from ref 28. ORTEP views of Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) and Os(CO)<sub>4</sub>(SbPh<sub>3</sub>) are given in Figures 1 and 2, respectively; these also give the labeling scheme employed for each molecule. Final coordinates of non-hydrogen atoms for Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) are given in Table IV, and for Os(CO)<sub>4</sub>(SbPh<sub>3</sub>) in Table V. Important bond lengths and angles for Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) are given in Table VII, for Os(CO)<sub>4</sub>(SbPh<sub>3</sub>) in Table VIII. Anisotropic thermal parameters for the non-hydrogen atoms, final positional and thermal parameters for hydrogen atoms, and structure factor listings are available as supplementary material. The computer programs used were those developed by Larsen and Gabe.<sup>29</sup>

**Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>).** Pale yellow crystals suitable for X-ray analysis were obtained by slow sublimation in a sealed, evacuated tube. Weissenberg photographs (Cu K $\alpha$ ,  $\lambda = 1.5418 \text{ \AA}$ ) were used to assign the space group as *R*3 or *R*3̄. The compound was then assumed to be isostructural with Fe(CO)<sub>4</sub>(SbMe<sub>3</sub>)<sup>30</sup> (space group *R*3) and the cell dimensions of this compound were used as a first approximation for the ruthenium analogue. Accurate cell dimensions were determined by least-squares refinement of 25 accurately centered reflections ( $2\theta = 20\text{--}25^\circ$ , Mo K $\alpha_1$ ,  $\lambda = 0.7093 \text{ \AA}$ ). Crystal data are given in Table II. Diffraction data were collected on an Enraf-Nonius CAD 4-F diffractometer at  $20 \pm 1^\circ \text{C}$ . (A graphite monochromator was used.) Background measurements were made by extending the scan range by 25% at each side of the scan. Measurement of two standard reflections every 1 h allowed monitoring of crystal decay and stability of the detection chain. Lorentz, polarization, and semiempirical absorption<sup>31</sup> corrections were made to the data.

The non-hydrogen positional parameters from Fe(CO)<sub>4</sub>(SbMe<sub>3</sub>)<sup>30</sup> were employed as the initial model. Refinement proceeded quickly by full-matrix least-squares methods with anisotropic temperature factors used in the final cycles. Hydrogen atoms were not included in the calculations. When inverse coordinates were used, the residual  $R_1$  dropped from 0.0248 to 0.0233, which indicated the original indexing to be incorrect; therefore, the correct coordinates were used for subsequent refinement. The weighting scheme,  $w = [\sigma^2(F) + 0.0006F^2]^{-1}$  was shown to be correct on the basis of trends in  $w\Delta^2$  as a function of  $|F_o|$  and  $(\sin \theta)/\lambda$ . The 110 reflection was omitted from the refinement because it suffered from extinction (final  $KF_o = 229.43$ ,  $F_c = 260.88$ ). Details of the data collection and final refinement parameters are given in Table III. Atomic scattering factors, which included anomalous dispersion, were taken from ref 28. An ORTEP view, with the labeling scheme, of Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>) is shown in Figure 3. Final coordinates for non-hydrogen atoms are given in Table VI, bond lengths and angles in Table IX. Anisotropic thermal parameters and a structure factor listing are

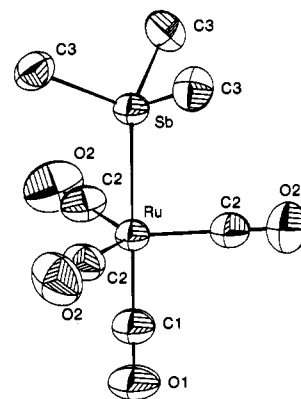


Figure 3. ORTEP diagram of ax-Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>).

available as supplementary material. The computer programs used in this determination were from ref 32.

**Os(CO)<sub>4</sub>(AsPh<sub>3</sub>).** Space group and approximate cell dimensions were determined analogous to those of Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>). Accurate cell dimensions were obtained in a manner similar to that used for Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>); the  $2\theta$  scan range was  $16.2\text{--}22.4^\circ$  for 25 accurately centered reflections. The standard deviations on the cell dimensions were slightly higher than desirable for data collection; an examination of the peak profiles also indicated the crystal was not of sufficient quality for a structure determination. Since the cell dimensions revealed the compound was isostructural with Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) the analysis was not pursued further.

## Results and Discussion

Several known and previously unknown complexes of the type  $M(\text{CO})_4(\text{L})$  ( $M = \text{Fe, Ru, Os}$ ;  $\text{L} = \text{group 15 ligand}$ ) have been prepared. The ruthenium-trimethylphosphine derivative, Ru(CO)<sub>4</sub>(PMe<sub>3</sub>), was prepared by the action of PMe<sub>3</sub> on Ru<sub>3</sub>(CO)<sub>12</sub> at  $120^\circ \text{C}$  under 75 atm of CO, a method used previously for Ru(CO)<sub>4</sub>[P(O)Me<sub>3</sub>].<sup>14</sup> The osmium compound may be prepared similarly only under more forcing conditions (see Experimental Section). All the other derivatives were prepared from  $M(\text{CO})_5$  and the appropriate ligand L in hexane. With Ru(CO)<sub>5</sub> the reaction proceeded at a convenient rate at room temperature, whereas for Os(CO)<sub>5</sub> temperatures of  $80^\circ \text{C}$  or above were necessary to affect similar rates of substitution. This illustrates the greater lability of carbonyls when bonded to a second-row transition metal, a property we have previously observed with this group of metals in the  $M(\text{CO})_4(\text{SiCl}_3)_2$  derivatives.<sup>33</sup> For osmium (and to a lesser extent ruthenium) there were competing reactions in the formation of the Os(CO)<sub>4</sub>(L) derivatives, which gave Os<sub>3</sub>(CO)<sub>12</sub> and other clusters. The yields of Os(CO)<sub>4</sub>(L) were improved by carrying out the reaction under several atmospheres of carbon monoxide. The yields, however, were still poor. The color of the derivatives ranged from the orange Ru(CO)<sub>4</sub>(SbPh<sub>3</sub>) to the white  $M(\text{CO})_4(\text{PMe}_3)$  complexes. They could be handled in air for short periods but decomposed upon prolonged exposure.

As mentioned in the Introduction, complexes of the type  $M(\text{CO})_4(\text{L})$  are usually trigonal bipyramidal with L in an axial site. Such complexes exhibit a characteristic pattern of three carbonyl stretches in the infrared spectrum.<sup>8</sup> Many of the complexes prepared in this study did indeed show this pattern (Table X, Figures 4 and 5). However, many exhibited additional bands indicative of the presence of a second species in solution (Table X). This second species was assigned to the trigonal-bipyramidal form of  $M(\text{CO})_4(\text{L})$  with the non-carbonyl ligand in an equatorial position. This was done on the basis of the solid-state structures of Os(CO)<sub>4</sub>(SbPh<sub>3</sub>) (reported below) and Ru(CO)<sub>4</sub>(SbPh<sub>3</sub>) reported by Forbes et al.<sup>19</sup> Both structures show that the SbPh<sub>3</sub> ligand occupies an equatorial site in the trigonal-bipyramidal coordination sphere. It is just these complexes that exhibit most of the second form in solution (Figure 4). Four carbonyl stretches

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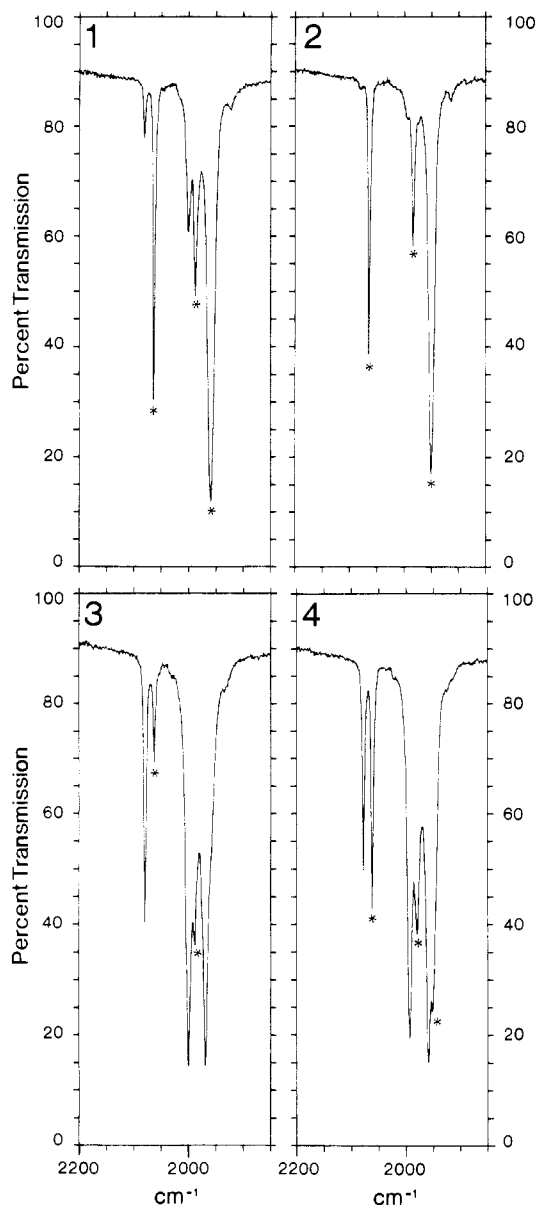
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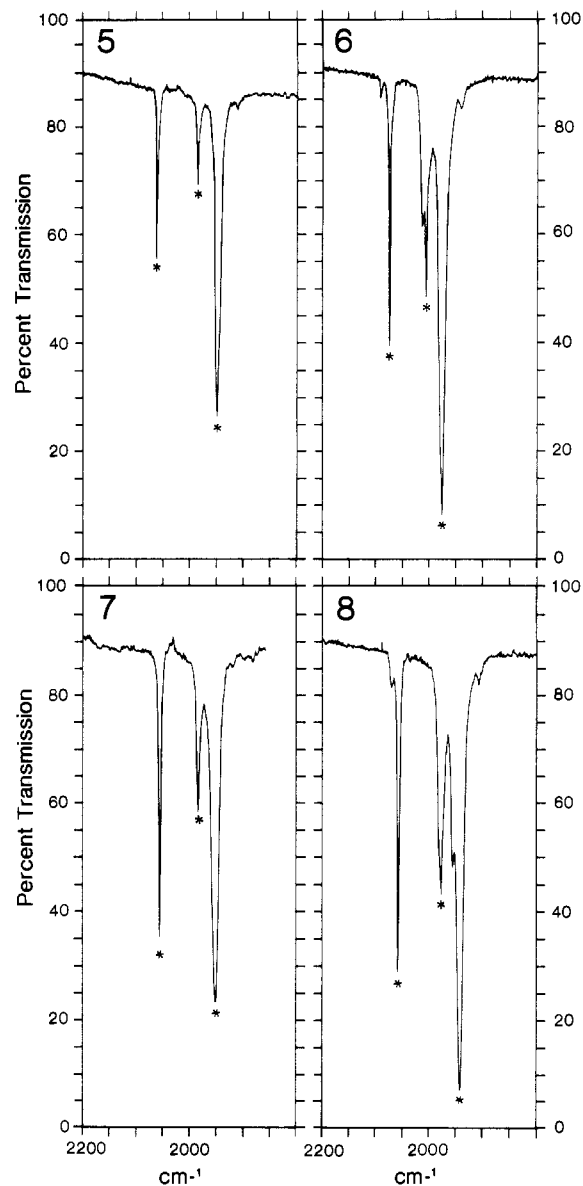
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**Figure 4.** Carbonyl stretching region of the infrared spectra of some  $M(\text{CO})_4(\text{EPh}_3)$  complexes in hexane: (1)  $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$ ; (2)  $\text{Os}(\text{CO})_4(\text{AsPh}_3)$ ; (3)  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$ ; (4)  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$ . (Bands assigned to the axial isomer are marked with an asterisk.)

are expected for the equatorial form of  $M(\text{CO})_4(\text{L})$  (of  $C_{2v}$  symmetry). Only a maximum of three such stretches could be unambiguously assigned as due to this form for the compounds reported here. However, in no case was the equatorial isomer present to the exclusion of the axial analogue so that the fourth band of the equatorial isomer may have been accidentally degenerate with a band of the axial compound. The solid-state infrared spectra of  $M(\text{CO})_4(\text{SbPh}_3)$  ( $M = \text{Ru}, \text{Os}$ ) did show four carbonyl resonances consistent with their solid-state geometry.<sup>34</sup> (Complexes of the type  $\text{eq-}M(\text{CO})_4(\text{alkene})$ <sup>8,35</sup> and the remarkable  $\text{eq-Fe}(\text{CO})_4[\text{P}[\text{OC}(\text{CF}_3)_2\text{CN}]_3]$ <sup>9</sup> exhibit four CO stretches.) Possible reasons for the formation of the equatorial isomer are presented after the discussion of the structures determined in this study.

The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of each complex exhibited only one carbonyl resonance at room temperature (Table X; coupling



**Figure 5.** Carbonyl stretching region of the infrared spectra of further  $M(\text{CO})_4(\text{L})$  complexes in hexane: (5)  $\text{Ru}(\text{CO})_4(\text{PMe}_3)$ ; (6)  $\text{Ru}(\text{CO})_4[\text{P}(\text{OCH}_2)_3\text{CMe}]$ ; (7)  $\text{Fe}(\text{CO})_4(\text{SbPh}_3)$ ; (8)  $\text{Os}(\text{CO})_4(\text{SbMe}_3)$ . (Again, bands assigned to the axial isomer are marked with an asterisk.)

to phosphorus was observed when L was a phosphorus-donor ligand). As found previously for complexes of this type,<sup>7,10,14,36,37</sup> this almost certainly indicated that there was rapid axial-equatorial exchange of the carbonyl ligands in a given isomer and that both isomers, in those cases where both isomers could be detected, were also in rapid equilibrium. The well-known Berry pseudorotation mechanism<sup>38</sup> for axial-equatorial exchange in pentacoordinate complexes can account for both these observations. In some  $\text{ax-Co}(\text{CO})_4(\text{X})$  derivatives, axial-equatorial carbonyl exchange was slowed sufficiently in solution at low temperatures such that separate  $^{13}\text{C}$  NMR resonances were observed for each type of carbonyl. The coalescence temperatures ranged from  $-10^\circ\text{C}$  (for  $\text{X} = \text{CF}_3$ ) to  $<-160^\circ\text{C}$  ( $\text{X} = \text{SnCl}_3$ ) and varied with the size of the ligand.<sup>37</sup> For this reason the solution  $^{13}\text{C}$  NMR spectrum of the ruthenium derivative with the smallest group 15 ligand ( $\text{P}(\text{OCH}_2)_3\text{CMe}$ ) was studied to  $-125^\circ\text{C}$ . However, the carbonyl resonance remained a singlet, coupled to phosphorus. The  $^{13}\text{C}$

(34) IR (KBr disk):  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$ ,  $\nu(\text{CO})$  2078 (m), 1997 (s), 1981 (s), 1949 (s)  $\text{cm}^{-1}$ ;  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$ ,  $\nu(\text{CO})$  2076 (m), 1987 (s), 1973 (s), 1937 (vs)  $\text{cm}^{-1}$ .

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(38) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

NMR spectra of  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  (at  $-120^\circ\text{C}$ ) and  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$  (at  $-117^\circ\text{C}$ ) in  $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$  similarly gave sharp singlets for the carbonyl resonance.<sup>39</sup>

For several compounds, the axial-equatorial equilibrium in hexane was studied down to  $-90^\circ\text{C}$  by infrared spectroscopy. However, in each case the change in the relative absorbances of the two highest energy CO stretches with temperature was insignificant, so that thermodynamic parameters for the equilibria could not be obtained.

**Structural Studies.** The structures of  $\text{Ru}(\text{CO})_4(\text{AsPh}_3)$ ,  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$ , and  $\text{Ru}(\text{CO})_4(\text{SbMe}_3)$  were determined by conventional X-ray diffraction techniques. ORTEP views of each molecule, along with the numbering scheme used, are given in Figures 1, 2, and 3 respectively; important bond lengths and angles are given in Table VII, VIII, and IX. As can be seen, in the ruthenium compounds the group 15 ligand occupies an axial site in the trigonal-bipyramidal coordination sphere of the metal, but in the osmium case the non-carbonyl ligand is in an equatorial position. (In the crystalline state  $\text{Os}(\text{CO})_4(\text{AsPh}_3)$  was isostructural with  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$ .) From a comparison of the infrared spectra of these  $\text{M}(\text{CO})_4(\text{L})$  molecules, and from their crystal structures, reported here and elsewhere,<sup>19</sup> it appears that the preferred isomer in solution is the form adopted in the solid state. All four compounds,  $\text{M}(\text{CO})_4(\text{AsPh}_3)$  ( $\text{M} = \text{Ru}, \text{Os}$ ; axial isomer) and  $\text{M}(\text{CO})_4(\text{SbPh}_3)$  ( $\text{M} = \text{Ru}, \text{Os}$ ; equatorial isomer) adopt the same space group ( $P\bar{1}$ ) in the solid-state so that packing forces probably do not significantly favor one isomer over the other in the crystalline state. The iron compounds,  $\text{ax-Fe}(\text{CO})_4(\text{EPh}_3)$  ( $\text{E} = \text{P}, \text{Sb}^{40}$ ) also adopt the  $P\bar{1}$  space group in the solid state.

Although the main interest in the structures reported here was to confirm the isomerism exhibited by these compounds, there are several other points of interest about them. The Os-Sb bond length of  $2.612(2) \text{ \AA}$ <sup>41</sup> appears to be the first reported in the literature for a molecular compound. It may be compared with those reported for  $\text{OsSb}_2$  ( $2.639 \text{ \AA}$  and  $2.644 \text{ \AA}$ )<sup>41</sup> and the Ru-Sb distance of  $2.623(4) \text{ \AA}$  in  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$ .<sup>19,43</sup> The Ru-Sb distance of  $2.619(1) \text{ \AA}$  found for  $\text{Ru}(\text{CO})_4(\text{SbMe}_3)$  may likewise be compared to these lengths. The Ru-As bond length ( $2.461(2) \text{ \AA}$ ) is somewhat longer than the Ru-As bond lengths in the literature, which are in the range  $2.401(3)$ – $2.445(2) \text{ \AA}$ ,<sup>44</sup> however, the literature values are for bidentate arsenic ligands in cluster compounds so that it is difficult to attach any significance to the difference. The distortion from tetrahedral geometry of the group 15 ligand has been noted and discussed before.<sup>19,40</sup> It is usually explained in terms of the E-C ( $\text{E} = \text{group 15 atom}$ ) bonds having enhanced p character, while the M-E bond has enhanced s character. In  $\text{ax-Co}(\text{CO})_4(\text{X})$  compounds it has usually been found that there is a pronounced bending of the equatorial carbonyls toward the non-carbonyl ligand.<sup>45</sup> In  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$  and  $\text{ax-Ru}(\text{CO})_4(\text{SbMe}_3)$  this bending although present is not as pronounced.

The angles about the central atom in the axially substituted derivatives studied here were close to that expected for trigonal-bipyramidal coordination. However, the angles in the equatorial plane of the osmium atom in  $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$  were

significantly distorted for this geometry (Table VIII). Virtually identical distortions were observed in  $\text{eq-Ru}(\text{CO})_4(\text{SbPh}_3)$ <sup>19</sup> (the compounds are isostructural<sup>46</sup>). These distortions may result from repulsions between the bonding electrons in the immediate coordination sphere of the metal. It would be expected that there would be more repulsion between the bonding electrons in the M-C bonds than between these electrons and those in the M-Sb bond. This is because the bonding electrons in the M-C bonds are closer to the metal nucleus and because they also have a  $\pi$  component. This would lead to an expansion of the C-M-C angle at the expense of the C-M-Sb angles, as observed. Such an explanation can account for the distortions observed in  $\text{Co}(\text{PPh}_2\text{Me})_2(\text{Cl})_2(\text{NO})$  (phosphines axial) where the Cl-Co-Cl angle was compressed to  $108.4^\circ$  whereas one of the Cl-Co-N angles was enlarged to  $134.3^\circ$ , with the other at  $117.3^\circ$ .<sup>47</sup> (The bonding electrons would be closer to cobalt in the Co-N bond than those in the Co-Cl bond.) There was no significant distortion in  $\text{eq-Mn}(\text{CO})_4(\text{NO})$ <sup>16</sup> in agreement with the similarity of the Mn-CO and Mn-NO bonds. The C(1)-Os-Sb angle in  $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$  was smaller than the C(2)-Os-Sb angle. This may be because it is prevented from opening out by the presence of the phenyl group in the equatorial plane (Figure 2). However, the inequality of seemingly equivalent angles was also present in  $\text{Co}(\text{PPh}_2\text{Me})_2(\text{Cl})_2(\text{NO})$  where there was no such group near the equatorial plane.<sup>47</sup>

**The Axial-Equatorial Switchover.** This study represents the first occasion where a site preference switchover for a closely related series of five-coordinate complexes has been observed. Steric or electronic ( $\sigma$  and/or  $\pi$ ) reasons might account for the switchover. Each of the possibilities is now discussed in turn.

Brown and co-workers have demonstrated that an  $\text{ER}_3$  ligand in a  $\text{M}(\text{CO})_4(\text{ER}_3)$  complex has closer contacts with the carbonyl groups when it is in an equatorial site vs. the axial position.<sup>37</sup> This is a consequence of the inability of an equatorial as opposed to an axial  $\text{ER}_3$  ligand to adopt a configuration that is completely staggered with respect to the carbonyls. We also find that the closest nonbonded contacts do indeed occur in the equatorial compound,  $\text{Os}(\text{CO})_4(\text{SbPh}_3)$  ( $\text{C}(1)\cdots\text{H}(12) = 3.09 \text{ \AA}$ ). Furthermore, calculations on a model of  $\text{eq-Os}(\text{CO})_4(\text{AsPh}_3)$  using coordinates from  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$  and  $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$  indicate two contacts between the group 15 ligand and carbonyls that are slightly less than the sum of the van der Waals radii for the atoms involved ( $\text{C}(1)\cdots\text{H}(12) = 2.79 \text{ \AA}$ ;  $\text{C}(4)\cdots\text{H}(36) = 2.83 \text{ \AA}$ ).<sup>48</sup> Within  $\text{ax-Ru}(\text{CO})_4(\text{AsPh}_3)$ , the comparable contacts are at this sum ( $\text{C}(3)\cdots\text{H}(26) = 3.16 \text{ \AA}$ ).<sup>49</sup>

However, there have been a small number of structures recently reported<sup>50-52</sup> of  $\text{Fe}(\text{CO})_4(\text{L})$  molecules in which L was an extremely bulky phosphorus ligand, which also adopted an equatorial site in the solid state, e.g.  $\text{eq-Fe}(\text{CO})_4[\text{PPh}(\text{PPh}_2)]$ <sup>51</sup> and  $\text{eq-Fe}(\text{CO})_4[\text{P}(\text{C}(\text{SiMe}_3)_2)[\text{N}(\text{SiMe}_3)_2]]$ .<sup>52</sup> This may indicate that the equatorial position is, in fact, sterically the least hindered when all interactions between the carbonyls and an asymmetric phosphorus ligand are considered. It should be reiterated that the non-carbonyl ligand in these molecules was exceptionally bulky;

- (39) It is unfortunate that a low-temperature limiting spectrum of these compounds was not observed. Because of the presence of both isomers, valuable mechanistic information could have been obtained from the mode of collapse of the signals.
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- (41) So as to be consistent with those bond lengths most often quoted in the literature, lengths in this discussion are uncorrected for riding motion. However, it should be noted that these lengths are significantly different from those that have been so corrected.
- (42) Kjekshus, A.; Rakke, T.; Anderson, A. F. *Acta Chem. Scand., Ser. A* **1977**, *A31*, 253.
- (43) On the basis of average Ru-Ru and Os-Os bond lengths in  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$ , covalent radii of the zerovalent metal ions are  $1.427 \text{ \AA}$  for Ru(0) and  $1.439 \text{ \AA}$  for Os(0): Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.
- (44) Lavigne, G.; Lukan, N.; Bonnet, J.-J. *Nouv. J. Chim.* **1981**, *5*, 423.
- (45) Roberts, P. J.; Trotter, J. *J. Chem. Soc. A* **1970**, 3246.
- (46) Berry, A. D.; Corey, E. R.; Hagen, A. P.; MacDiarmid, A. G.; Saalfeld, F. E.; Wayland, B. B. *J. Am. Chem. Soc.* **1970**, *92*, 1940.

- (46) The structure of  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  was solved in the nonstandard space group  $B1$ .<sup>19</sup> A Delaney reduction of the reported cell dimensions to space group  $P\bar{1}$  gave the following values:  $a = 11.131$ ,  $b = 11.285$ ,  $c = 12.775 \text{ \AA}$ ;  $\alpha = 129.12$ ,  $\beta = 102.24$ ,  $\gamma = 102.57^\circ$ .
- (47) Brock, C. P.; Collman, J. P.; Dolcetti, G.; Farnham, P. H.; Ibers, J. A.; Lester, J. E.; Reed, C. A. *Inorg. Chem.* **1973**, *12*, 1304.
- (48) These calculations did not allow for reorientation of the atoms within the molecule so as to minimize these contacts.
- (49) The closest nonbonded contacts between the hydrogens and oxygens were:  $\text{O}(1)\cdots\text{H}(32) = 3.02 \text{ \AA}$  for  $\text{ax-Ru}(\text{CO})_4\text{AsPh}_3$ , and  $\text{O}(1)\cdots\text{H}(12) = 3.04 \text{ \AA}$  for  $\text{eq-Os}(\text{CO})_4(\text{SbPh}_3)$ .
- (50) Flynn, K. M.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 2085. Flynn, K. M.; Hope, M.; Murray, B. D.; Olmstead, M. M.; Power, P. P. *Ibid.* **1983**, *105*, 7750. Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Organometallics* **1984**, *3*, 1044.
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- (52) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* **1984**, *3*, 1132.



even  $P(t\text{-Bu})_3$  (cone angle<sup>53</sup> = 182°) in  $\text{Fe}(\text{CO})_4[P(t\text{-Bu})_3]$  adopts an axial position in the solid state.<sup>54</sup> The cone angles of the group 15 ligands studied here<sup>55</sup> were much less than this value, and therefore, the steric interactions would be much less important.

Notwithstanding which position is the most sterically hindered, it can be seen from Table X that cases exist where both a large or a small group 15 ligand gives some of the equatorial isomer, e.g.  $\text{eq-Ru}(\text{CO})_4(\text{SbPh}_3)$  (large ligand) and  $\text{eq-Ru}(\text{CO})_4[P(\text{OCH}_2)_3\text{CMe}]$  (small ligand). Furthermore, the iron complexes studied here, where steric factors should be the most important, exist only as the axial isomer even though the non-carbonyl ligand had a range of sizes. Cases of  $\text{eq-Fe}(\text{CO})_4(\text{L})$  compounds have been reported for situations when L is small (e.g.  $\text{L} = \text{PF}_3$ )<sup>7</sup> and large (e.g.  $\text{L} = \text{P}(\text{OC}(\text{CF}_3)_2\text{CN})_3$ )<sup>9</sup>. If the equatorial position is more hindered, it would be expected that  $\text{Ru}(\text{CO})_4(\text{SbMe}_3)$  should form more of the equatorial isomer than  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$ . In fact, the reverse is the case in solution (Figures 4 and 5), and in the solid state the trimethyl derivative crystallizes as the axial isomer (Figure 3) whereas the phenyl analogue crystallizes as the equatorial form (Figure 2). On the other hand, if the axial position is the more hindered, it is hard to rationalize on steric arguments that  $\text{Fe}(\text{CO})_4(\text{SbPh}_3)$  and  $\text{Ru}(\text{CO})_4(\text{PPh}_3)$  exist as the axial isomer as the only detectable configuration but that for  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  the equatorial isomer is the major form. Although steric factors may be important in determining the site preference of ligands in hindered five-coordinate molecules, it is concluded that for the present series of molecules that such factors are relatively unimportant.

As can be seen from Table X, the tendency to give the equatorial isomer is  $\text{Ph}_3\text{Sb} > \text{Ph}_3\text{As} > \text{Ph}_3\text{P}$ . It is usually assumed that in five-coordinate organometallic complexes the better  $\pi$ -acceptor ligand adopts the equatorial position.<sup>15</sup> The CO stretching frequencies of  $\text{Ru}(\text{CO})_4[P(\text{OCH}_2)_3\text{CMe}]$  and  $\text{Ru}(\text{CO})_4(\text{PF}_3)$ <sup>17</sup> have high values, which is consistent with the fact that these phosphorus ligands are good  $\pi$  acceptors. The occurrence of the equatorial isomer for these molecules may be rationalized by using  $\pi$ -bonding arguments. However, the spectroscopic data (Table X) are not consistent with the triphenylstibine ligand having exceptional  $\pi$ -acceptor properties. The CO stretching frequencies of the  $\text{M}(\text{CO})_4(\text{EPh}_3)$  ( $\text{E} = \text{P}, \text{As}, \text{Sb}$ ) complexes (axial isomer) are all very similar, which suggests the  $\pi$ -acceptor abilities of the  $\text{EPh}_3$  ligands are similar (a conclusion reached by other workers<sup>56,57</sup>). The results certainly do not indicate that  $\text{SbPh}_3$  is a superior  $\pi$  acceptor to CO. Such arguments cannot, therefore, be used to explain why  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  exists predominantly as the equatorial isomer.

Rossi and Hoffmann have concluded that, for  $d^8$  complexes such as these, the stronger  $\sigma$  donor would prefer the axial position, or conversely, the weaker  $\sigma$  donor would favor the equatorial site.<sup>1</sup> A similar conclusion was reached by Burdett by use of angular overlap methods.<sup>2</sup> The present results may be rationalized in terms of the  $\sigma$ -donor ability of the various ligands in these molecules. Most experimental evidence<sup>57-59</sup> indicates that the donor ability of group 15 molecules follows the order  $\text{P} > \text{As} > \text{Sb}$ . If the donor ability of CO were greater than that of  $\text{Ph}_3\text{Sb}$ , then an order  $\text{Ph}_3\text{P} > \text{Ph}_3\text{As} > \text{CO} > \text{Ph}_3\text{Sb}$  for the donor strength (in transition-metal complexes) could explain the occurrence of the equatorial isomers in the ruthenium and osmium derivatives. (Although the CO stretching frequencies in  $\text{M}(\text{CO})_4(\text{L})$  molecules should change with the  $\sigma$ -donor properties of L, it is not expected to be as marked

as the change with  $\pi$  properties.<sup>60</sup> That the order  $\text{Me}_3\text{P} > \text{Me}_3\text{As} > \text{CO} \approx \text{SbMe}_3$  is possible is suggested by the heats of formation of  $\text{L}\cdot\text{BX}_3$  adducts (in  $\text{kcal mol}^{-1}$ , from L and  $\text{BX}_3$ ):<sup>58</sup>  $\text{Me}_3\text{P}\cdot\text{BH}_3$ , -79.9;  $\text{Me}_3\text{As}\cdot\text{BH}_3$ , -49.6;  $\text{OC}\cdot\text{BH}_3$ , -25.1;<sup>61</sup>  $\text{Me}_3\text{Sb}\cdot\text{BCl}_3$ , -26.8<sup>58</sup> (anomalous reaction with  $\text{BH}_3$ )<sup>62</sup>. It would be expected that  $\text{Ph}_3\text{Sb}$  would be a poorer donor than  $\text{Me}_3\text{Sb}$ . This would also explain why an axial-equatorial changeover for the preferred isomer occurred between  $\text{Ru}(\text{CO})_4(\text{SbMe}_3)$  and  $\text{Ru}(\text{CO})_4(\text{SbPh}_3)$  (Figures 2 and 3) although reasons based on the  $\pi$ -acceptor properties of the stibines involved cannot be completely ruled out.

On the basis of the <sup>13</sup>C chemical shifts exhibited by the carbonyls in  $\text{Ni}(\text{CO})_3(\text{L})$  complexes an order of  $\text{SbPh}_3 > \text{PPh}_3 > \text{AsPh}_3$  has been suggested for the donor-acceptor properties of these ligands.<sup>63</sup> However, the differences in the chemical shifts were small, and alternative orderings for these ligands can be obtained from the chemical shifts reported for other  $\text{M}(\text{CO})_n(\text{L})$  complexes.<sup>63,64</sup> Also, from the data given<sup>63</sup> for the  $\text{Ni}(\text{CO})_3$ - $(\text{EMe}_3)$  derivatives an order of  $\text{PMe}_3 > \text{SbMe}_3 > \text{AsMe}_3$  for the donor-acceptor properties was indicated. The iron compounds reported here (Table X), which exist as the axial isomer as the only detectable form, give an order of  $\text{AsPh}_3 > \text{SbPh}_3 > \text{PPh}_3$  if this method is employed.<sup>65</sup> In view of the poor understanding<sup>66</sup> of the <sup>13</sup>C NMR chemical shifts of transition-metal complexes, conclusions based on them should be treated with caution especially if the complexes contain heavy atoms such as antimony. It is interesting that a <sup>13</sup>C NMR study of  $\text{W}(\text{CO})_5(\text{L})$  derivatives did give an order of  $\text{Ph}_3\text{P} > \text{Ph}_3\text{As} > \text{Ph}_3\text{Sb}$  for the donor strengths based on the <sup>1</sup>J(<sup>183</sup>W-<sup>13</sup>C) (trans) coupling constants.<sup>64</sup>

A structural investigation of  $\text{Cr}(\text{CO})_5(\text{EPh}_3)$  ( $\text{E} = \text{Group 15 element}$ ) concluded from an analysis of the Cr-E s character and bond order on going down the periodic table, i.e.  $\text{P} < \text{As} < \text{Sb} < \text{Bi}$ .<sup>67</sup> Although it is generally accepted that a shorter bond length is indicative of a stronger bond, we suggest that this may not be the case for some Lewis acid-base adducts of group 15 elements. Bryan and Kuczkowski concluded that  $\text{Me}_3\text{P}\cdot\text{BH}_3$  was a more stable adduct than  $\text{F}_3\text{P}\cdot\text{BH}_3$  even though the latter molecule had a significantly shorter P-B bond.<sup>68</sup> Similarly, in  $\text{PtCl}_2(\text{PEt}_3)(\text{PF}_3)$  the Pt- $\text{PEt}_3$  bond length (2.272 (3) Å) was longer than the Pt- $\text{PF}_3$  length (2.141 (3) Å) even though the Pt- $\text{PF}_3$  bond was thought to have lower intrinsic strength than the Pt- $\text{PEt}_3$  bond.<sup>69</sup> Although not explicitly stated, other workers have implied that bonds of metal to trialkylphosphines may be stronger than metal to  $\text{PF}_3$  linkages even though the bond lengths would indicate the opposite conclusion.<sup>70</sup> A recent theoretical study<sup>71</sup> found that the highest occupied molecular orbital on  $\text{PMe}_3$  and  $\text{PF}_3$  was mainly an s-p hybrid with that on the fluoro molecule containing more s character (29%) than that on the methyl analogue (11%), in

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accordance with Bent's rule.<sup>72</sup> The lone pair on PF<sub>3</sub> was found to be more compact and at a lower energy than that on PMe<sub>3</sub>, consistent with the basic properties of these molecules. It therefore appears possible that a dative bond could be shorter but nevertheless weaker than a second such bond, e.g. M-PF<sub>3</sub> vs. M-PMe<sub>3</sub>. Nonbonding repulsions might also prevent ideal overlap in short bonds of this type. For these reasons arguments relating bond strength to bond length of donor-acceptor bonds may not always be applicable.

From Table X and Figures 4 and 5 it can be seen that the tendency of the transition metals to give the equatorial isomer was Ru > Os >> Fe. (In fact, there was no example for the group 15 ligands studied here of a Fe(CO)<sub>4</sub>(L) molecule that gave detectable amounts of the equatorial form in solution.) Without a detailed analysis of the bonding in these molecules it is difficult to rationalize this trend especially for the ruthenium and osmium complexes where the energy differences between the two isomers were small. To a first approximation, the relative  $\sigma$ -donor ability of the carbonyl and group 15 ligands would not be expected to change with the transition metal and, therefore, the proportion of equatorial isomer should not change with a change in central atom.

As previously stated Rossi and Hoffmann have shown theoretically that the better  $\pi$ -acceptor ligand should prefer the equatorial site in a d<sup>8</sup> M(CO)<sub>4</sub>(L) complex.<sup>1</sup> The trend observed here may be rationalized by using  $\pi$ -bonding arguments, if the  $\pi$ -acceptor ability of CO to the metal follows the order Fe >> Os > Ru. For the iron derivatives studied here, the preference of the CO ligand for the equatorial site arising from its  $\pi$ -acceptor properties could then outweigh the preference of the weak-donor group 15 ligand for that site. From Figure 5 (spectrum 7) it can be seen that even Fe(CO)<sub>4</sub>(SbPh<sub>3</sub>) shows no detectable equatorial isomer in solution. For the examples reported in the literature of equatorial Fe(CO)<sub>4</sub>(L) complexes where L was a moderately sized group 15 ligand, the non-carbonyl group had good  $\pi$ -acceptor properties, i.e. Fe(CO)<sub>4</sub>(PF<sub>3</sub>)<sup>7</sup> and Fe(CO)<sub>4</sub>(P[OC(CF<sub>3</sub>)<sub>2</sub>CN]<sub>3</sub>).<sup>9</sup> The high CO stretching frequencies exhibited by these compounds was consistent with this idea. From conventional bonding arguments, if the amount of  $\pi$  bonding follows the order Fe-CO > Os-CO > Ru-CO, the CO stretching frequencies should be in the reverse order, i.e. Ru-CO > Os-CO > Fe-CO. There is some evidence for this (Table X), but the differences are not great. These small differences were also seen in the stretching frequencies of the parent pentacarbonyls.<sup>20</sup> Pentacarbonylruthenium had the highest CO stretching frequencies and was also the least stable of the three carbonyls.<sup>20</sup> This may reflect a smaller  $\pi$  component in the Ru-CO bond. The effect of the lanthanide contraction on osmium could explain why the  $\pi$  bonds to CO are stronger to this metal than to ruthenium.<sup>75</sup> (Relativity effects<sup>76</sup> for osmium should

increase the  $\sigma$  component but weaken the  $\pi$  component of osmium to ligand bonds.)

### Conclusions

It is usually found that good donor ligands are poor  $\pi$  acceptors and vice versa. Changes that occur in molecular geometry, or some other property, when a good donor ligand is replaced by one with good  $\pi$ -acceptor character are difficult to unambiguously attribute as due to changes in the  $\sigma$  or  $\pi$  bonding within the molecule. The group 15 molecules EPh<sub>3</sub>, where E = P, As, or Sb, are, therefore, a useful series of ligands in that their  $\pi$  properties, and sizes, are similar, but the basicity decreases markedly on going to the member lower in the periodic table. Some of the trigonal-bipyramidal molecules of the series M-(CO)<sub>4</sub>(EPh<sub>3</sub>) (M = Fe, Ru, Os) exhibited axial-equatorial isomerism; the tendency to give the equatorial isomer was Sb > As > P. This observation has therefore been rationalized that the weaker  $\sigma$ -donor ligand had a greater preference for the equatorial site. Although this result has been predicted theoretically, we believe this is the first time it has been corroborated experimentally. Ligand  $\pi$ -bonding properties are considered important in the determination of the site preference of the ligand L in M(CO)<sub>4</sub>(L) complexes. They may be important in the present molecules since arguments based on  $\pi$  bonding can rationalize the different tendencies of the central atom to give the equatorial isomer (Ru > Os >> Fe). They can also be used to explain why Ru(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe] exists to some extent as the equatorial isomer. However, some caution is required with this interpretation for Ru(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe] since it is expected that the phosphite ligand is also a weak donor, and this may be most important factor in determining the site preference in this molecule.

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**Registry No.** *ax*-Ru(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe], 97170-88-2; *eq*-Ru(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe], 97233-20-0; *ax*-Ru(CO)<sub>4</sub>(PMe<sub>3</sub>), 97233-17-5; *ax*-Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>), 85848-64-2; *eq*-Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>), 85781-13-1; *ax*-Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>), 97170-89-3; *eq*-Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>), 97233-19-7; *ax*-Os(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe], 97170-90-6; *eq*-Os(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe], 97233-21-1; *ax*-Os(CO)<sub>4</sub>(PMe<sub>3</sub>), 97233-18-6; *ax*-Os(CO)<sub>4</sub>(AsPh<sub>3</sub>), 85848-66-4; *eq*-Os(CO)<sub>4</sub>(AsPh<sub>3</sub>), 85781-14-2; *ax*-Os(CO)<sub>4</sub>(SbMe<sub>3</sub>), 97170-91-7; *eq*-Os(CO)<sub>4</sub>(SbMe<sub>3</sub>), 97233-22-2; *ax*-Os(CO)<sub>4</sub>(SbPh<sub>3</sub>), 85848-67-5; *eq*-Os(CO)<sub>4</sub>(SbPh<sub>3</sub>), 85781-15-3; *ax*-Fe(CO)<sub>4</sub>(PMe<sub>3</sub>), 18475-02-0; *ax*-Fe(CO)<sub>4</sub>[P(OCH<sub>2</sub>)<sub>3</sub>CMe], 97170-92-8; *ax*-Fe(CO)<sub>4</sub>(PPh<sub>3</sub>), 35679-07-3; *ax*-Fe(CO)<sub>4</sub>(AsPh<sub>3</sub>), 35644-25-8; *ax*-Fe(CO)<sub>4</sub>(SbPh<sub>3</sub>), 35917-16-9; *ax*-Ru(CO)<sub>4</sub>(PPh<sub>3</sub>), 33635-52-8; *ax*-Ru(CO)<sub>4</sub>(SbPh<sub>3</sub>), 85848-65-3; *eq*-Ru(CO)<sub>4</sub>(SbPh<sub>3</sub>), 71356-99-5; Os(CO)<sub>4</sub>(PPh<sub>3</sub>), 33635-53-9; Ru(CO)<sub>5</sub>, 16406-48-7; Os(CO)<sub>5</sub>, 16406-49-8.

**Supplementary Material Available:** Tables of bond lengths and angles for the phenyl groups of Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) and Os(CO)<sub>4</sub>(SbPh<sub>3</sub>), final temperature factors for Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>), structure factors for Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>), Os(CO)<sub>4</sub>(SbPh<sub>3</sub>), and Ru(CO)<sub>4</sub>(SbMe<sub>3</sub>), and hydrogen atom coordinates for Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) and Os(CO)<sub>4</sub>(SbPh<sub>3</sub>) (46 pages). Ordering information is given on any current masthead page. Thermal parameters for Ru(CO)<sub>4</sub>(AsPh<sub>3</sub>) and Os(CO)<sub>4</sub>(SbPh<sub>3</sub>) have been previously deposited.<sup>21</sup>

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(73) Arguments based on the hardness of metals and ligands<sup>74</sup> might lead to the conclusion that the soft SbPh<sub>3</sub> ligand should form stronger bonds to ruthenium and osmium than to iron. This in turn would lead to the prediction that there would be less of the equatorial form for the M-(CO)<sub>4</sub>(SbPh<sub>3</sub>) derivatives of the heavier metals. This is, of course, contrary to what is observed.

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