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Communications

Axial-Equatorial Isomerism in the Pentacoordinate Complexes $M(CO)_4(EPh_3)$ (M = Fe, Ru, Os; E = P, As, Sb)

Sir:

Most crystallographic studies on complexes of the type $M(CO)_4L$ (M = Fe, Ru; L = group 5A donor ligand) reveal approximate trigonal-bipyramidal geometry about the transition metal with the noncarbonyl ligand in an axial position.[1,2] The case of $Ru(CO)_4(SbPh_3)$ is, therefore, unusual in that the structure determination shows the triphenylstibine group occupies an equatorial site in the solid state.[3] We have now synthesized $Ru(CO)_4(AsPh_3)$, $Os(CO)_4(AsPh_3)$, and $Os(CO)_4(SbPh_3)$ along with the other, previously known,[3,4] members of the series $M(CO)_4(EPh_3)$ (M = Fe, Ru, Os; E = P, As, Sb), by the reaction of $M(CO)_5$ with the appropriate ligand.[5] The crystal structures of $Ru(CO)_4(AsPh_3)$ and $Os(CO)_4(SbPh_3)$ have been determined;[8] in the former compound the noncarbonyl ligand occupies an axial site whereas in the latter it adopts an equatorial position (Figures 1 and 2). Furthermore, $Os(CO)_4(AsPh_3)$ was isostructural with its ruthenium analogue.[9]

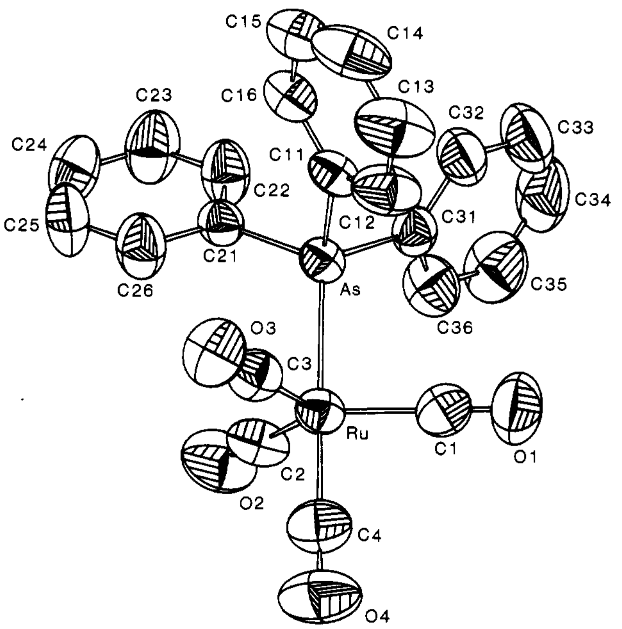

Figure 1. ORTEP diagram of $Ru(CO)_4(AsPh_3)$. Bond lengths (Å): Ru–As, 2.461 (1); Ru–C(1), 1.918 (5); Ru–C(2), 1.915 (5); Ru–C(3), 1.921 (5); Ru–C(4), 1.890 (5). Bond angles (deg): As–Ru–C(4), 178.5 (2); C(1)–Ru–C(2), 117.9 (2); C(2)–Ru–C(3), 123.4 (2); C(3)–Ru–C(1), 118.5 (2); Ru–As–C(mean), 115.2.

Table I. Infrared Spectra (Carbonyl Region) of $M(CO)_4(EPh_3)$ Complexes[a]

compd	eq[b]	ax.[c]	eq	ax.	eq	ax.
$Fe(CO)_4(PPh_3)$		2052		1979		1947
$Fe(CO)_4(AsPh_3)$		2051		1977		1947
$Fe(CO)_4(SbPh_3)$		2048		1976		1946
$Ru(CO)_4(PPh_3)$		2062		1988		1955
$Ru(CO)_4(AsPh_3)$	2079	2061	1999	1986		1958
$Ru(CO)_4(SbPh_3)$	2078	2060	1999	1987	1967	
$Os(CO)_4(PPh_3)$		2061		1983		1946
$Os(CO)_4(AsPh_3)$	2077	2061	1991	1981		1947
$Os(CO)_4(SbPh_3)$	2076	2060	1992	1978	1957	1950

[a] All spectra recorded in hexane. [b] Equatorial isomer. [c] Axial isomer.

The infrared spectra, in the carbonyl region, of this series of complexes are consistent with the presence of *both* axial and equatorial isomers in solution for the cases with M = Ru, Os and E = As, Sb (Figure 3, Table I).[10] The single carbonyl ^{13}C NMR resonance (207.7 ppm) observed for $Ru(CO)_4(SbPh_3)$ in $CFCl_2H$ solution at −115 °C strongly suggests the two isomers are in rapid equilibrium on the NMR time scale. (Five-coordinate metal carbonyl derivatives are invariably

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(1) (a) Favas, M. C.; Kepert, D. L. *Prog. Inorg. Chem.* **1980**, *27*, 325. (b) Riley, P. E.; Davis, R. E. *Inorg. Chem.* **1980**, *19*, 159. (c) Cowley, A. H.; Davis, R. E.; Remadna, K. *Ibid.* **1981**, *20*, 2146.

(2) Cobbledick, R. E.; Einstein, F. W. B.; Pomeroy, R. K.; Spetch, E. R. *J. Organomet. Chem.* **1980**, *195*, 77.

(3) Forbes, E. J.; Jones, D. L.; Paxton, K.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1979**, 879.

(4) (a) Reckziegel, A.; Bigorgne, M. *J. Organomet. Chem.* **1965**, *3*, 341. (b) Darensbourg, D. J. *Inorg. Chim. Acta* **1970**, *4*, 597. (c) Albers, M. O.; Coville, N. J.; Ashworth, T. V.; Singleton, E. *J. Organomet. Chem.* **1981**, *217*, 385. (d) L'Eplattenier, F.; Calderazzo, F. *Inorg. Chem.* **1968**, *7*, 1290.

(5) The pentacarbonyls of ruthenium and osmium have been described in the literature.[6] For an improved synthesis of these compounds, see ref 7. Preparation of $Ru(CO)_4L$ derivatives was carried out in a manner similar to that described for $Ru(CO)_4[P(OMe)_3]$.[2] The osmium compounds were synthesized at 90 °C under 20 atm of CO.

(6) Calderazzo, F.; L'Eplattenier, F. *Inorg. Chem.* **1967**, *6*, 1220.

(7) Rushman, P.; van Buuren, G. N.; Shiralian, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693.

(8) Structures were solved by conventional X-ray diffraction techniques. Crystal data for $Ru(CO)_4(AsPh_3)$: space group $P1$; $a = 10.605$ (3), $b = 11.068$ (4), $c = 9.980$ (3) Å; $\alpha = 113.57$ (3), $\beta = 93.14$ (3), $\gamma = 91.47$ (3)°; $Z = 2$; $R = 0.020$, $R_w = 0.021$ for 1650 reflections with $I > 2.3\sigma(I)$. Crystal data for $Os(CO)_4(SbPh_3)$: space group $P1$; $a = 11.123$ (2), $b = 11.284$ (4), $c = 12.714$ (4) Å; $\alpha = 129.29$ (2), $\beta = 102.35$ (2), $\gamma = 102.45$ (2)°; $Z = 2$; $R = 0.019$, $R_w = 0.021$ for 3115 reflections with $I > 2.3\sigma(I)$.

(9) Crystallographic data for $Os(CO)_4(AsPh_3)$: $a = 10.633$ (6), $b = 11.029$ (7), $c = 9.979$ (6) Å; $\alpha = 113.43$ (5), $\beta = 93.24$ (5), $\gamma = 91.60$ (5)°.

(10) The original report of $Ru(CO)_4(SbPh_3)$ incorrectly ascribed all the infrared-active CO stretches observed for this compound in solution as due to the equatorial isomer.[3]

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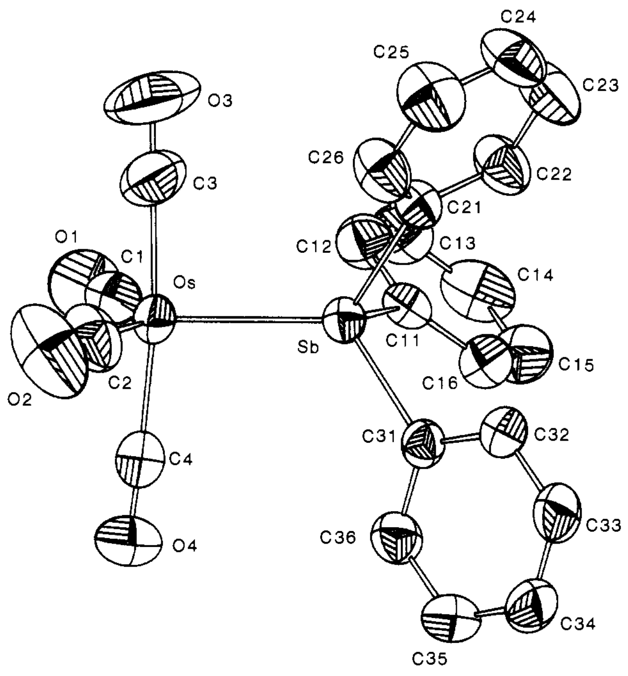

Figure 2. ORTEP diagram of $Os(CO)_4(SbPh_3)$. Bond lengths (Å): Os–Sb, 2.612 (2); Os–C(1), 1.926 (6); Os–C(2), 1.911 (7); Os–C(3), 1.953 (6); Os–C(4), 1.939 (6). Bond angles (deg): C(3)–Os–C(4), 173.8 (3); Sb–Os–C(1), 107.0 (2); C(1)–Os–C(2), 136.4 (3); C(2)–Os–Sb, 116.6 (2); Os–Sb–C(mean), 117.9.

stereochemically nonrigid.[2,11])

This represents the first time where a site preference switchover for a closely related series of five-coordinate complexes has been observed. The reasons for the switchover are not clear. As can be seen from Table I, the tendency to give the equatorial isomer is $Ph_3Sb > Ph_3As > Ph_3P$. It is usually assumed that in five-coordinate organometallic complexes the better π-acceptor ligand adopts the equatorial position.[12] However, the spectroscopic data are not consistent with the triphenylstibine ligand as having exceptional π-acceptor properties. The CO stretching frequencies of the $M(CO)_4(EPh_3)$ complexes (axial isomer) are all very similar, which suggests the π-acceptor ability of the EPh_3 ligands are similar (a conclusion reached by other workers[13,14]). The results certainly do not indicate that $SbPh_3$ is a superior π acceptor to CO.

Rossi and Hoffmann concluded that, for d^8 complexes such as these, the weaker σ-donor ligand would also favor the equatorial position,[15] a conclusion similarly reached by Burdett by use of angular-overlap methods.[16] The present results could be rationalized in terms of the σ-donor ability of the various groups. Most experimental evidence[14,17,18] (but not all[19]) indicates the donor ability of group 5 ligands follow the order P > As > Sb. If the donor ability of CO were greater than that of Ph_3Sb, then an order of $Ph_3P > Ph_3As > CO > Ph_3Sb$[20] for the donor strength (in transition-metal complexes) could explain the occurrence of equatorial isomers in the present series of compounds. (Although the CO stretching frequencies in $M(CO)_4L$ molecules should change with the σ-donor properties of L, it is not expected to be as marked as the change with π properties.[22]) On the other hand, it may be that steric factors are responsible for the preference of the axial isomer for those complexes with short M–E distances since the equatorial position for the ER_3 ligand is the more sterically hindered.[11] The closest intramolecular contacts between the group 5 ligand and the carbonyls within $Ru(CO)_4(AsPh_3)$ and $Os(CO)_4(SbPh_3)$ are at the sum of the van der Waals radii for the atoms involved (closest contact: C(1)···H(12) = 3.04 Å in $Os(CO)_4(SbPh_3)$). However, calculations on a model of the equatorial isomer of $Os(CO)_4(AsPh_3)$, using coordinates from $Ru(CO)_4(AsPh_3)$ and $Os(CO)_4(SbPh_3)$, do indicate two contacts that are slightly less than this sum (C(1)···H(12) = 2.79 Å; C(4)···H(36) = 2.83 Å).[23] These interactions may

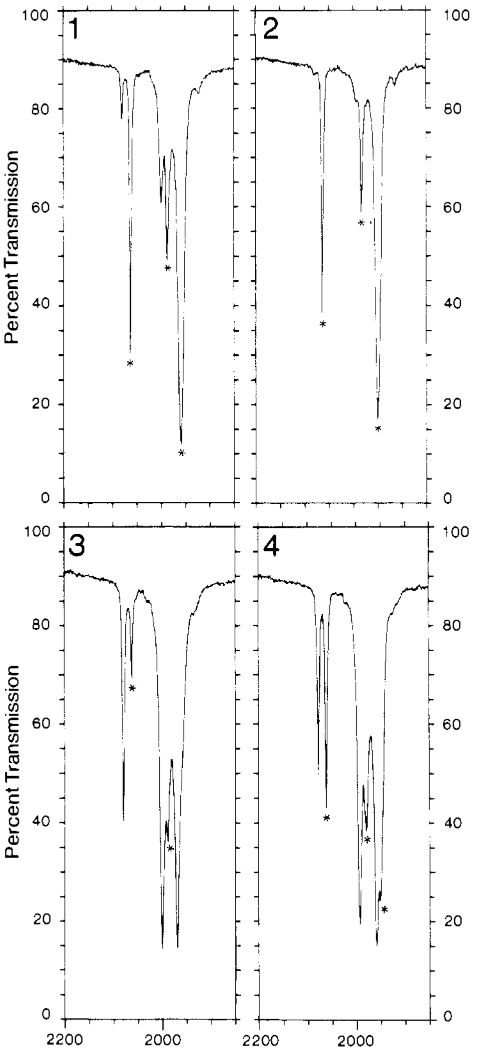

Figure 3. Carbonyl stretching region of the infrared spectra of some $M(CO)_4(EPh_3)$ complexes in hexane: (1) $Ru(CO)_4(AsPh_3)$; (2) $Os(CO)_4(AsPh_3)$; (3) $Ru(CO)_4(SbPh_3)$; (4) $Os(CO)_4(SbPh_3)$. (Bands assigned to the axial isomer are marked with an asterisk.)

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(11) Lichtenberger, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 8187.

(12) (a) Udovich, C. A.; Clark, R. J.; Haas, H. *Inorg. Chem.* **1969**, *8*, 1066. (b) Shapley, J. R.; Osborn, J. A. *Acc. Chem. Res.* **1973**, *6*, 305. (c) Churchill, M. R.; Lin, K. G. *J. Am. Chem. Soc.* **1974**, *96*, 76. (d) Goldfield, S. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 770.

(13) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; p 89.

(14) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 105.

(15) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

(16) Burdett, J. K. *Inorg. Chem.* **1976**, *15*, 212.

(17) Mente, D. C.; Mills, J. L.; Mitchell, R. E. *Inorg. Chem.* **1975**, *14*, 123.

(18) (a) Mente, D. C.; Mills, J. L. *Inorg. Chem.* **1975**, *14*, 1862. (b) Debies, T. P.; Rabalais, J. W. *Ibid.* **1974**, *13*, 308. (c) Manzer, L. E.; Tolman, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 1955.

(19) (a) Carty, A. J.; Taylor, N. J.; Coleman, A. W.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 639. (b) Bodner, G. M.; May, M. P.; McKinney, L. E. *Inorg. Chem.* **1980**, *19*, 1951.

(20) Such an order is suggested by the heats of formation of $L{\cdot}BX_3$ adducts (in kcal mol^{-1}, from L and BX_3): $Me_3P{\cdot}BH_3$, −79.9; $Me_3As{\cdot}BH_3$, −49.6; $Me_3Sb{\cdot}BBr_3$, −19.8 (anomalous reaction with BH_3); $OC{\cdot}BH_3$, −25.1.[17,21]

(21) Ermler, W. C.; Glasser, F. D.; Kern, C. W. *J. Am. Chem. Soc.* **1976**, *98*, 3799 and references therein.

(22) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975; p 172.

be sufficient to account for the preference of the axial form of $Os(CO)_4(AsPh_3)$ over the equatorial isomer. Experiments are currently under way in an attempt to distinguish between these two possible explanations for the switchover.

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Registry No. *ax*-$Fe(CO)_4(PPh_3)$, 35679-07-3; *ax*-$Fe(CO)_4(AsPh_3)$, 35644-25-8; *ax*-$Fe(CO)_4(SbPh_3)$, 35917-16-9; *ax*-$Ru(CO)_4(PPh_3)$, 33635-52-8; *eq*-$Ru(CO)_4(AsPh_3)$, 85781-13-1; *ax*-$Ru(CO)_4(AsPh_3)$, 85848-64-2; *eq*-$Ru(CO)_4(SbPh_3)$, 71356-99-5; *ax*-$Ru(CO)_4(SbPh_3)$, 85848-65-3; *ax*-$Os(CO)_4(PPh_3)$, 33635-53-9; *eq*-$Os(CO)_4(AsPh_3)$, 85781-14-2; *ax*-$Os(CO)_4(AsPh_3)$, 85848-66-4; *eq*-$Os(CO)_4(SbPh_3)$, 85781-15-3; *ax*-$Os(CO)_4(SbPh_3)$, 85848-67-5; $Ru(CO)_5$, 16406-48-7; $Os(CO)_5$, 16406-49-8.

Supplementary Material Available: Listings of final positional and thermal parameters with standard deviations for $Ru(CO)_4(AsPh_3)$ and $Os(CO)_4(SbPh_3)$ (4 pages). Ordering information is given on any current masthead page.

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(23) These calculations did not allow for reorientation of the atoms within the molecule so as to minimize these contacts.

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A Dinuclear Platinum(II) Complex Containing a Bridging Tridentate Triphosphorous Acid Derivative $[((EtO)_2PO)_2P(O)]^-$

Sir:

The reactivity of P–OR and P–Cl bonds is such that reactions between triorgano phosphites or chlorophosphines and transition-metal complexes may often cause a transformation of the phosphorus donor ligand as well as the expected coordination. Examples are the well-documented degradation of triorgano phosphites, $[P(OR)_3]$, to phosphonato ligands, $P(O)(OR)_2$,[1] and the recent transformation of trimethyl phosphite to the unusual $P(OMe)_2$[2,3] and $P(OMe)$[4] ligands. Reactions in which phosphorus(III) compounds condense and coordinate to form diphosphito ligands are also known, for example, in the formation of the bidentate bridging diphosphito ligand $-O_2POPO_2-$ from the solid-state reaction of phosphorous acid with a platinum(II) salt.[5] A very recent communication[6] also advances evidence for the formation of higher homologues of this ligand, but fully characterized examples involving more than two condensed phosphorus units are unknown. Indeed tri- and polyphosphites are very rare even in simple phosphorus chemistry.[7] We now wish to report that in the course of studying the reactions of tetraethyl diphosphite, $[(EtO)_2POP(OEt)_2]$, and of chlorodiethoxyphosphine, $[PCl(OEt)_2]$, with platinum complexes we have established the formation of a ligand derived from the unknown triphosphorous acid, $[H_5P_3O_7]$.

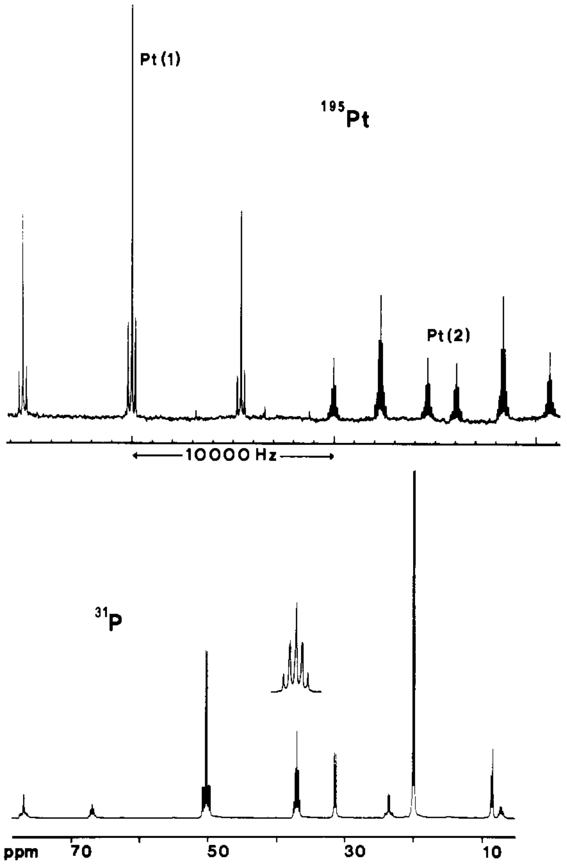

Figure 1. $^{195}Pt\{^1H\}$ and $^{31}P\{^1H\}$ nuclear magnetic resonance spectra of complex **1**.

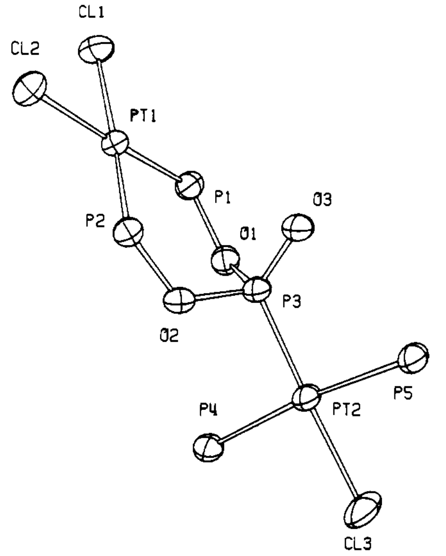

Figure 2. ORTEP plot of the molecular structure of complex **1**. The ethoxy groups on P(1) and P(2) and the ethyl groups on P(4) and P(5) have been omitted for clarity.

Addition of $[(EtO)_2POP(OEt)_2]$ (0.10 mL) to a stirred solution of *trans*-$[Pt_2Cl_4(PEt_3)_2]$ (0.30 g) in dichloromethane (15 mL) at 25 °C under an atmosphere of dry nitrogen,

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(1) Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* **1970**, 2080.

(2) Choi, H. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 153.

(3) Day, V. W.; Tavanaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657.

(4) Fernandez, J. M.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1981**, 2250.

(5) Sperline, R.; Dickson, M. K.; Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1977**, 62. Dos Remedios Pinto, M. A. F.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **1980**. 13.

(6) Dickson, M. K.; Fordyce, W. A.; Appel, D. M.; Alexander, K.; Stein, P.; Roundhill, D. M. *Inorg. Chem.* **1982**, *21*, 3857.

(7) Toy, A. D. F. In "Comprehensive Inorganic Chemistry"; Bailar, J. C., Emeleus, H. J., Nyholm, R., Trotman-Dickenson, A. F., Eds.; Pergamon Press: Oxford, 1973; Vol. 2, p 475.

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