× $10^{-5}$ M were obtained by reduction of I with ascorbic acid or via eq 4 by mixing equimolar solutions of Ru(NH$_3$)$_3$BPA$_2^{2+}$

$$
\text{Ru}^{II}(\text{NH}_3)_2\text{BPA}^{2+} + \text{Fe}^{II}(\text{CN})_5\text{BPA}^{-} = 3 \text{k}_a \text{k}_d
$$

(4)

(prepared by reduction of Ru$^{III}$)$\text{NH}_3\text{BPA}^{3+}$ with ascorbic acid and Fe$^{II}(\text{CN})_5\text{BPA}^{3-}$) and solutions of demonstrate the MLCT bands of both Ru(II) and Fe(II) centers (Table I). Values of $k_d = (2.1 \pm 0.1) \times 10^{-3}$ M$^{-1}$ s$^{-1}$ were measured by a competitive method (490 nm) [4-acetylpyridine] = $2.3 \times 10^{-3}$ M and [Ru(NH$_3$)$_3$BPA$_2^{2+}$] = (1.5-10) $\times 10^{-3}$ M. Values of $k_d = (1.9 \pm 0.1) \times 10^{-3}$ s$^{-1}$ were measured by the same procedure as for $k_d$. When solutions are mixed with excess S$_2$O$_8^{2-}$, biphasic kinetics are observed at 410 nm. The first rapid change corresponds to oxidation of 3 to 1 with a rate constant of $(5.0 \pm 0.2) \times 10^{-4}$ M$^{-1}$ s$^{-1}$. The second, slower change corresponds to oxidation of 1 to 2 with $k_d = (4.6 \pm 0.3) \times 10^{-3}$ M$^{-1}$ s$^{-1}$, in acceptable agreement with the value reported above.

Rate constants for the peroxodisulfate oxidations of Ru$^{II}$, (NH$_3$)$_3$BPA$^{3+}$, Fe$^{II}(\text{CN})_5$BPA$^{-}$, and (NH$_3$)$_3$Rh$^{II}(\text{BPA})$Fe$^{II}$- (CN)$_4^{2-}$, and relevant reduction potentials (cyclic voltammetry) are presented in Table I.

Peroxodisulfate discriminates by a factor of 10$^6$ in its reactions with Ru$^{II}$, (NH$_3$)$_3$BPA$^{3+}$ and Fe$^{II}(\text{CN})_5$BPA$^{-}$ (Table I). Therefore, the oxidation of 3 to 1, which proceeds at a rate comparable with that of Ru$^{II}$, (NH$_3$)$_3$BPA$^{3+}$, undoubtedly involves electron loss from Ru(II). On the basis of present and earlier reactivity patterns, it is apparent that the oxidation of 1 proceeds at an anomalously high rate for removal of an electron from a Fe(II) center. The ca. 10$^3$ difference between 1 and (NH$_3$)$_3$Rh$^{II}$-(BPA)Fe$^{II}$-(CN)$_4^{2-}$ is particularly noteworthy since the two complexes have equal charges, geometry, and $E^0$ values. We propose that the oxidation of 1 proceeds via rapid and reversible isomerization to 1' (eq 5) and is followed by reaction of 1' with S$_2$O$_8^{2-}$

$$
\text{(NH}_3\text{)}_3\text{Ru}^{III}\text{(BPA)}\text{Fe}^{II}\text{(CN)}_5
$$

(eq 6). In this interpretation, $k_1 = k_3 k_4$, $k_5$, estimated from $1' + \text{S}_2\text{O}_8^{2-} \rightarrow 2 + \text{SO}_4^{2-} + \text{SO}_2^{2-} k_d$ (6)

$E^0$ values of 0.44 and 0.29 V for reduction of Fe(III) and Ru(III) centers, respectively, is $2.9 \times 10^{-3}$. Therefore, $k_5 = (1.5 \times 10^{5}$ M$^{-3}$ s$^{-1}$, a perfectly reasonable value for a Ru(II) center. The key finding herein, namely, that the electron to be lost from a given site is first transferred (in a rapid pre-equilibrium) to a site which is oxidized more readily, could have important implications in biological electron-transport chains.

Facile Substitution of Triphenylphosphine in Wilkinson's Catalyst by Sn(NBu)$_3$SiMe$_2$ Syntheses and Molecular Structures of Square-Planar and Homoleptic Trigonal-Bipyramidal Stannylene Complexes of Rhodium(1)

It has been known for some time that certain tin(II) compounds, such as SnCl$_4$, Sn(acac)$_2$, and Sn[N(SiMe$_3$)$_2$)$_2$, are excellent ligands for late transition elements—particularly those of the platinum-metal group. The monomeric, divalent tin species bear some resemblance, both in structure and reactivity, to carbones and thus the name stannylene has been proposed for these compounds.

A considerable portion of the research in our group has been concerned with synthesis and chemical characterization of the cyclic bis(amino)stannylene 1 and its lighter and heavier homologs. The presence of both a filled $d$-donor orbital and an
empty low-lying σ-acceptor orbital on the tin atom of monomeric 1 suggests electronic similarities to PR3 (R = Alkyl, phenyl) and to a certain extent to the isolobal C0.6

Here we report on our initial results of the controlled reactions between the classical platinum-metal complex RHCl(PPh3)3 and 1. Our findings suggest that 1 is as good a ligand as any of the previously reported tin(II) compounds and that it may rival tertiary phosphines as ligand for soft acids.

The addition of exactly 2 equiv of 1 to a RHCl(PPh3)3 suspension in toluene at –20 °C leads to the rapid formation of a single product in high yield. Only one doublet ( –109.9 ppm, chemical shift relative to external P(OMe)3, with shifts to high field 2.571 (2) A, and Rh−Sn(2) = 2.577 (2) A. Despite apparent chemical equivalence the rhodium-phosphorus bond lengths are decidedly different (Rh−P(1) 2.273 (4) A, and Rh−P(2) = 2.238 (4) A), a feature we ascribe to the distortion of the plane. As can be seen in Figure 1, 2 crystallizes in a highly distorted square-planar cis geometry. Thus the plane defined by RH−P−(1)−P(2) is twisted by 15.8° relative to the plane defined by the three metal atoms. Complex 2 may be considered to be derived from RHCl(PPh3)3 through the formal insertion of one stannylene unit into the Rh−Cl bond of the coordinatively unsaturated RHCl(PPh3)3 − known to be present in solution—followed by the subsequent coordination of a second moiety of 1. The most peculiar structural feature of 2 is the presence of a chlorine-bridged, chelating bis(stannylene) ligand. This fragment is somewhat reminiscent of the Sn2Cl4 complex anion. It is presumably the presence of this Sn−Cl−Sn bridge that has led to the formation of only the cis isomer, despite the greater steric strain brought on by this configuration. The perspective view in Figure 1 demonstrates the symmetrical coordination of the chlorine atom through the empty p orbitals of the tin atoms. Both metal–metal bond distances in 2 are equal within experimental error: Rh−Sn(1) = 2.571 (2) A, and Rh−Sn(2) = 2.577 (2) A. Despite apparent chemical equivalence the rhodium–phosphorus bond lengths are decidedly different (Rh−P(1) = 2.273 (4) A and Rh−P(2) = 2.238 (4) A), a feature we ascribe to the distortion of the plane.

When reaction 1 is allowed to continue at room temperature, the formation of a second product, at the expense of 2, is observed by NMR techniques. This new compound, 3, is also produced, in nearly quantitative yield, according to eq 2. NMR spectral evidence (1H, 31P) shows 3 to be free of PPh3 and to contain the cyclic bis(aminostannylene) 1 as its only ligand. The comparatively mild conditions employed in reaction 2 have thus led to the complete substitution of triphenylphosphine by 1. An air-sensitive dark red crystal of the toluene solvate (2-toluene)2

As can be seen in Figure 1, 2 crystallizes in a highly distorted square-planar cis geometry. Thus the plane defined by RH−P−(1)−P(2) is twisted by 15.8° relative to the plane defined by the three metal atoms. Complex 2 may be considered to be derived from RHCl(PPh3)3 through the formal insertion of one stannylene unit into the Rh−Cl bond of the coordinatively unsaturated RHCl(PPh3)3 − known to be present in solution—followed by the subsequent coordination of a second moiety of 1. The most peculiar structural feature of 2 is the presence of a chlorine-bridged, chelating bis(stannylene) ligand. This fragment is somewhat reminiscent of the Sn2Cl4 complex anion. It is pre-

Figure 1. Perspective drawing of 2. Phenyl rings of PPh3 and hydrocarbons have been omitted for clarity. Selected dimensions (not mentioned in text): Sn(1)−Rh−P(2) = 160.1 (1)°; Sn(2)−Rh−P(1) = 161.8 (1)°; Sn(1)−Rh−Sn(2) = 83.3 (1)°; P(1)−Rh−P(2) = 97.3 (1)°; average N−Sn−N = 75.6 (4)°; average Sn−N = 2.06 (1) Å; average Si−N = 1.73 (1) Å.
presence of this chelating bis(stannylene) unit dominates the relative orientation of the remaining ligands. There are two distinct trends in the Rh-Sn bond distances. First, one can observe the expected longer metal-metal bonds of four-coordinate vs three-coordinate tin. Second, the rhodium–tin bond distances of the equatorial ligands are shorter than those of the axial stannylene. This latter feature is in line with the general trends observed in complexes have been reported, although accounts of studies on pounds containing rhodium-tin bonds have been known for only 25 years; few of these have been X-ray structurally characterized. To our knowledge, no homoleptic trinodal-bipyramidal Rh/Sn complexes have been reported, although accounts of studies on the structurally similar \[\text{[Rh(SnCl}_3\text{)}_4\text{SnCl}_4]\] and P~(SICI~)~* have appeared in the literature. In summary, the cyclic stannylene I seems to be a highly useful ligand in its ability to stabilize low-valent metal complexes. The facile replacement of PPh~3~ by 1 is particularly noteworthy, since SnCl~2~ apparently does not react with RhCl(PPh~3~)~2~ at all. Platinum-metal/tin(II) chloride mixtures are known to be useful catalysts for a number of industrial processes, and our efforts toward understanding the bonding in these interesting complexes and their chemical behavior are continuing.

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Supplementary Material Available: An Experimental Section, ORTEP drawings and complete atomic numbering schemes for 2.2-toluene and drawings and complete atomic numbering schemes for 2.2-toluene and 3-toluene, and tables of crystallographic parameters, final positional and anisotropic thermal parameters for non-hydrogen atoms, isotropic thermal parameters, bond lengths, and bond angles for the two structures (16 pages); tables of observed and calculated structure factors (36 pages).

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Synthesis, Structure, and Reactivity of Cerium(III) Alkoxides. 2. Thermal Decomposition of Ce(OC'O'Bu)_3

and the Structure of Ce(OC'O'Bu)_3H

Well-characterized homoleptic metal alkoxides are of considerable interest as precursors to metal oxides. Both thermolytic and hydrolytic methods have been employed to convert alkoxides to the corresponding oxides. Little, however, is known concerning the mechanistic steps involved in the thermal decomposition of metal alkoxides, especially those that lack accessible \(\beta\)-hydrogen atoms. This contrasts with extensive mechanistic information available for the decomposition of the corresponding metal alkyls.

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Figure 1. The molecular structure of 3 drawn with 40% probability thermal ellipsoids. Distances: Ce–O(1), 2.363 (3) Å; Ce–O(2), 2.142 (2) Å; Ce–O(3), 2.152 (3) Å; Ce–O(4), 2.143 (3) Å. Angles: O(1)–Ce–O(1'), 115.4 (1)°; O(1)–Ce–O(2), 115.4 (1)°; O(1)–Ce–O(3), 114.0 (1)°; O(2)–Ce–O(3), 113.3 (1)°; O(2)–Ce–O(4'), 107.8 (1)°; O(3)–Ce–O(1'), 126.7 (1)°; Ce–O(1)–Ce', 105.7 (1)°.

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(1) See references cited in ref 12b and 15.


(4) While a similar reaction was reported for a bimetallic system, the mechanism of decomposition was not examined; see: (a) Hvoslef, J.; Hope, H.; Murray, B. D.; Power, P. J.; J. Am. Chem. Soc. 1983, 105, 107, 1196. (b) Anderson, G. K.; Clark, H. C.; Davis, J. A. Inorg. Chem. 1983, 22, 427. (b) Anderson, G. K.; Clark, H. C.; Davies, J. A. Ibid. 1983, 22, 434.


(6) 'H NMR (C6D6) (25 °C) (ppm): 31.5 (br, terminal OCi+Bu2); -18.0 (br, bridging OCHLBu2). The resonance due to bridging OCHLBu2 could not be located. The broadness of the spectrum was due to the paramagnetic Ce(III) ion. This compound was also independently synthesized by the reaction of Ce[N(SiMe3)]3 with 3 equiv of HOCiPBu3 in pentane.