The orbitals and terms (C_{2v}, A-frame systems) relevant to the analysis of the low-energy electronic transitions in these systems are shown in Figure 3. In this model, the y axis is chosen as the metal-metal axis. Transition assignments based upon this orbital scheme, similar to the schemes for C_{2h}, D_{2h}, and D_{4h} Rh(I) and Ir(I) binuclear systems employed by Mann et al.,[5] Fordyce and Crosby,[2] and Kenney et al.[3] are as follows: phosphorescence, $^3B_2 \rightarrow {}^1A_1$; fluorescence, $^1B_2 \rightarrow {}^1A_1$; absorption, $^1A_1 \rightarrow {}^1B_2$. We have chosen our axis system to agree with the assignments of Marshall et al. for the room-temperature luminescence from $[Ir(\mu\text{-pz})(COD)]_2$ (pz is pyrazolyl; COD is 1,5-cyclooctadiene).[6]

In the proposed model, the ground-state metal-metal bond order is formally zero; a bond order of 1.0 is predicted for the lowest excited singlet and triplet configurations. These A-frame Rh(I) molecules represent another group of d^8 square-planar bridged systems in which the molecules are predicted to contract when excitation occurs.[2,3,7]

The $^3B_2$ excited term yields A_1, B_1, and A_2 spin-orbit states; the A_2 state cannot couple with the A_1 ground state by an electronic dipole mechanism. From a correlation with the states of more symmetrical systems[2] this forbidden component is predicted to be the lowest component in the triplet manifold; thus, it can be predicted that the phosphorescence lifetimes of these A-frame complexes should mimic the behavior of the more symmetrical D_{2h} rhodium complexes and become exceedingly long (milliseconds) at temperatures below 10 K.[2] Temperature-dependent lifetime studies are planned.

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Registry No. $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$, 67202-35-1; $[Rh_2(CO)_2Cl(dam)_2]BPh_4$, 70561-97-6.

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Hydrostannolysis Reactions of $M_2(NMe_3)_6$ (M = W, Mo)

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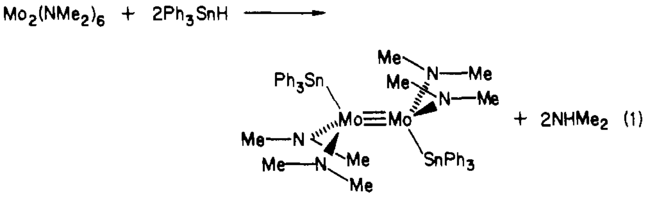
Interest in heterometallic transition-metal complexes containing metal-metal bonds has grown recently. Examples include transition metal–transition metal,[1] transition metal–post transition metal,[2] and transition metal–main group metal[3] bonds. Part of this interest arises from the frequent use of main-group metals as "promoters" of heterogeneous transition-metal catalysts.[4] An interesting homogeneous example is the hydroformylation catalyst formed from mixtures of Pt complexes and $SnCl_2$.[5]

As part of our interest in this area we have examined the reaction of tin hydrides with tungsten and molybdenum alkoxides and amides with the aim of displacing alcohols or amines and forming M–Sn bonds. This type of process is referred to as hydrostannolysis and has been successfully used for the preparation of Sn–Sn[6] and M–Sn (M = Ti, Zr)[7] bonds. In this work we find that hydrostannolysis reactions of the tungsten and molybdenum amides $M_2(NMe_2)_6$ yield complexes containing one and two M–Sn bonds. The singly substituted Sn complexes $M_2(Ph_3Sn)(NMe_2)_5$ (**2**), are rare examples of isolatable complexes of this type with different coordination environments at each metal center.[8]

Results and Discussion

Preparation and Characterization of 1,2-$Mo_2(Ph_3Sn)_2(NMe_2)_4$. Yellow $Mo_2(NMe_2)_6$ reacts rapidly with 2 equiv of Ph_3SnH in chlorobenzene to give an orange solution. Orange crystals of 1,2-$Mo_2(Ph_3Sn)_2(NMe_2)_4$ (**1**) deposit on standing (eq 1).



1

At 30 °C the ^1H NMR spectrum of **1** shows signals for the phenyl rings and two signals for the NMe_2 groups. When the sample is warmed, the NMe_2 signals coalesce ($\Delta G^{\ddagger}$ = 70.3 kJ/mol at T_c = 80 °C). Such temperature-dependent behavior is typical[9] of rotationally hindered NMe_2 groups where each methyl group can be either proximal or distal to the M–M triple bond (see the structure shown in eq 1). Closely related complexes, 1,2-$M_2(NMe_2)_4(Sn(SnMe_3)_3)_2$, were prepared by treating $M_2Cl_2(NMe_2)_4$ with $LiSn(SnMe_3)_3$ and show similar NMR behavior ($\Delta G^{\ddagger}$ = 68.8 and 70.6 kJ/mol for M = Mo and W, respectively.[10] The ^{119}Sn spectrum of **1** shows a single tin resonance at 6.7 ppm ($SnMe_4$ reference).

Preparation and Characterization of $M_2(Ph_3Sn)(NMe_2)_5$. When $W_2(NMe_2)_6$ is treated with excess Ph_3SnH, a slow reaction occurs and the only product obtained is $W_2(Ph_3Sn)(NMe_2)_5$ (**2a**, eq 2). None of the doubly substituted product (the tungsten equivalent of **1**) is formed. The analogous molybdenum complex **2b** can be prepared by the reaction of $Mo_2(NMe_2)_6$ with 1 equiv of Ph_3SnH.

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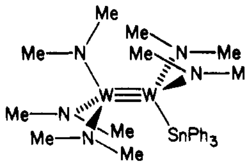
$W_2(NMe_2)_6 + Ph_3SnH \longrightarrow$



$+ NHMe_2$ (2)

2a

At 30 °C the ^1H NMR spectra of **2a** and **2b** show four methyl signals in a ratio of 2:2:4:2. The highest and lowest field signals are similar to those observed in the spectrum of **1** and are attributed to the NMe_2 proximal and distal methyl groups of the $M(NMe_2)_2(SnPh_3)$ half of the molecule. As in **1**, these coalesce when the sample is warmed ($\Delta G^{\ddagger} = 68.3$ kJ/mol at $T_c = 90$ °C for **2a**).

The other two signals observed at 30 °C are attributed to the freely rotating NMe_2 groups of the $M(NMe_2)_3$ half of the molecule. The smaller signal is the group anti to $SnPh_3$ (across the M–M triple bond). If the sample is heated, these two signals sharpen but do not exchange. The absence of any exchange indicates that there is no rotation about the M–M triple bond (up to 95 °C). When the sample is cooled, these signals collapse and two pairs of low-field and high-field signals appear with $\Delta G^{\ddagger} = 47.2$ ($T_c = -30$ °C) and 38.9 ($T_c = -73$ °C) kJ/mol for **2a** and $\Delta G^{\ddagger} = 45.2$ ($T_c = -40$ °C) and 38.4 ($T_c = -76$ °C) kJ/mol for **2b**. The smallest value in each set corresponds to the anti-to-$SnPh_3$ group. In comparison, the parent complex $M_2(NMe_2)_6$, which the $M(NMe_2)_3$ half of **2a** and **2b** should resemble, has $\Delta G^{\ddagger} = 46.9$ kJ/mol.[11]

Similar behavior was observed in solution for $M_2Cl(NMe_2)_5$; however, this complex could not be isolated because of facile disproportionation to 1,2-$M_2Cl_2(NMe_2)_4$ and $M_2(NMe_2)_6$.[12] Other unsymmetrical complexes of this type are 1,1-$Mo_2X_2(CH_2SiMe_3)_4$ (X = Br, Me, NMe_2, O-*t*-Bu, O-*i*-Pr),[13] and 1,1′-$Mo_2(NMe_2)(O_2CNMe_2)(CH_2SiMe_3)_4$.[11]

An X-ray diffraction study of **2b** was attempted. The only solvent found to give good-quality crystals was dimethoxyethane. However, a space group determination showed these to be trigonal with a cell volume requiring the molecule to have at least a threefold axis—impossible for **2b**. Data collection proceeded on the chance that it was a disorder problem for which a solution could be found and that it was not a case of twinning. (^1H NMR spectra of the dissolved crystals were identical with those of the original material.) Patterson and direct methods were applied with no success, both giving triangular groups of peaks separated by unreasonably short distances (~1.5 Å). No disorder model was found, and the attempt was abandoned.

Kinetics of Reaction 2. The kinetics of reaction 2 were investigated under pseudoorder conditions of excess Ph_3SnH in toluene-d_8 at 0 °C. The reaction was followed by ^1H NMR monitoring of the growth of the $HNMe_2$ peak. As the reaction progressed, we encountered problems from the catalytic decomposition of the tin hydride by the liberated amine. In addition to a significant decrease in the hydride concentration, the precipitated tin products interfered with the integration required for the kinetic analysis. Plots of ln ($P_\infty - P_t$) vs. time (P_t and P_∞ are the integrated peak intensity at time t and at time infinity, respectively) with a 10-fold and a 20-fold excess of Ph_3SnH showed considerable scatter and some curvature. Consistent with a continuous decrease in the hydride concentration during the run, the curvature was most noticeable for the 20-fold excess, which had the greatest amount of hydride decomposition. Assuming the reaction is first order in $W_2(NMe_2)_6$ and first order in Ph_3SnH, the plots gave an estimated second-order rate constant of 1×10^{-4} M^{-1} s^{-1} with reasonable agreement between the two hydride concentrations.

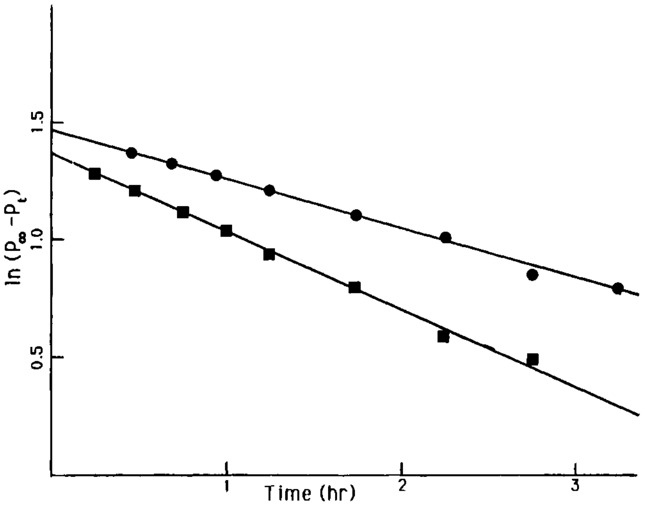


Figure 1. Pseudo-first-order plots of data obtained for reaction 2 (0.024 M $W_2(NMe_2)_6$): ●, 10-fold excess of Ph_3SnH; ■, 15-fold excess of Ph_3SnH.

Improved results were obtained by decreasing the initial concentrations of $W_2(NMe_2)_6$ and Ph_3SnH (less decomposition of the hydride) and by dropping the unreliable later time data where the hydride decomposition is significant. Since P_∞ is also dropped, values were estimated by the Kezdy–Swinbourne method.[14] Plots of the early time data for a 10-fold and a 15-fold excess of Ph_3SnH using the estimated P_∞ values are shown in Figure 1. These plots confirm the second-order kinetics of the reaction and give an average second-order rate constant of 1.54×10^{-4} M^{-1} s^{-1} with excellent agreement between the two Ph_3SnH concentrations (1.53×10^{-4} M^{-1} s^{-1} for the 10-fold excess and 1.56×10^{-4} M^{-1} s^{-1} for the 15-fold excess). As a check on our results, a multivariable least-squares computer analysis was applied to the early time data with P_0 (the time-zero peak integration), P_∞, and k' (the pseudo-first-order rate constant) as variables in the equation $P_t = (P_0 - P_\infty) \exp(-k't) + P_\infty$. The results of the two methods were in good agreement.

In more polar $CDCl_3$ the rate increased and the reaction was too fast to follow by NMR spectroscopy. Similar observations were made on hydrostannolysis reactions involving the formation of Sn–Sn bonds.[6] A polar intermediate or transition state involving electrophilic attack of the hydride hydrogen on the nitrogen lone pair of the amide group was suggested and appears reasonable here as well. Consistent with this, the less electrophilic hydride Me_3SnH cannot be substituted for Ph_3SnH in reaction 1 or 2. Nor can $M_2(O\text{-}t\text{-}Bu)_6$, with the less basic alkoxide groups, be substituted for $M_2(NMe_2)_6$.

Reactions of 1 and 2. Both **1** and **2** react with *t*-BuOH, Me_3SiCl, CO_2, and O_2. With *t*-BuOH no products could be isolated from the room-temperature reactions with ≥1 equiv. Heating **1** with 9 equiv of *tert*-butyl alcohol at 80 °C for 12 h gave as the only isolatable product $Mo_2(O\text{-}t\text{-}Bu)_6$, the same product obtained with $Mo_2(NMe_2)_6$.[15] With trimethylsilyl chloride and CO_2 no isolatable products were obtained. NMR spectra of the reaction mixtures suggested a mixture of products. The parent complexes, $M_2(NMe_2)_6$, react cleanly with *t*-BuOH to give $M_2(O\text{-}t\text{-}Bu)_6$ and $HNMe_2$,[15] with Me_3SiCl to give 1,2-$M_2(NMe_2)_4Cl_2$ and Me_3SiNMe_2,[12] and with CO_2 to give $M_2(CO_2NMe_2)_6$.[16]

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Concluding Remarks

The hydrostannolysis reaction is an effective means of forming tin–transition metal bonds. However, the reaction can be expected to be limited to complexes of ligands with significant basicity on the ligand atom bonded to the metal. Otherwise, electrophilic attack by the tin hydride will not occur. This, as well as steric reasons, is probably why the reactions studied here stop after the replacement of two NMe$_2$ groups. As the π-donating amide groups are replaced by the SnPh$_3$ groups, there is less competition for π-donation and the remaining amide groups lose more of their electron density to the metal. This deactivates them to hydrostannolysis. In the reactions of M(NMe$_2$)$_4$ (M = Ti, Zr) with tin hydrides, the only other known examples of a hydrostannolysis reaction of a transition-metal amide complex, complete substitution was observed but the reaction conditions were comparatively severes and the yields were low.[7]

Experimental Section

General Procedures. Experiments were performed under a dinitrogen atmosphere in a VAC drybox or by Schlenk techniques. Solvents were dried and purified by standard techniques under dinitrogen. M$_2$(NMe$_2$)$_6$,[11] M$_2$(O-*t*-Bu)$_6$,[17] Ph$_3$SnH,[18] and Me$_3$SnH[18] were prepared by literature procedures. CP grade gases were used as received.

NMR shifts are reported in ppm referenced to Me$_4$Si for ^{1}H (90 MHz) and ^{13}C (22.6 MHz) and to external SnMe$_4$ for ^{119}Sn (111.9 MHz). The ^{13}C and ^{119}Sn spectra were obtained in the ^{1}H-decoupled mode. The NMR spectra were run at 35 ± 5 °C except where noted. Microanalyses were performed by Schwarzkopf or Galbraith Microanalytical Laboratories using drybox techniques.

Preparation of 1,2-Mo$_2$(NMe$_2$)$_4$(SnPh$_3$)$_2$ (1). A solution of Ph$_3$SnH (1.17 g, 3.33 mmol) in 1 mL of chlorobenzene was added dropwise with stirring to a solution of Mo$_2$(NMe$_2$)$_6$ (0.73 g, 1.67 mmol) in chlorobenzene (5 mL). Stirring was stopped, and the mixture was allowed to stand for 3 h, during which time orange crystals precipitated. The crystals were removed by filtration, washed with 2 × 3 mL of pentane, and dried in vacuo (1.24 g). A second crop of 0.30 g was obtained by combining the pentane wash with the filtrate and cooling to −40 °C for 12 h; total yield 1.54 g (87%). An analysis sample was prepared by recrystallization from CH$_2$Cl$_2$/pentane. The resulting crystals lost solvent of crystallization on exposure to vacuum. ^{1}H NMR (C$_6$D$_6$): 7.48–7.17 (m, 15, SnPh$_3$), 3.93 (s, 6, NMe$_2$), 2.68 (s, 6, NMe$_2$′). The two NMe$_2$ signals collapse and coalesce as the temperature is raised; T_c = 80 °C and $\Delta G^\ddagger$ = 63 kJ/mol^{-1}. ^{119}Sn NMR: 6.7 (s, $\Delta\nu_{1/2}$ = 70 Hz). Anal. Calcd for MoC$_{22}$H$_{27}$N$_2$Sn: C, 49.47; H, 5.10; N, 5.25. Found: C, 49.23; H, 5.20; N, 5.23.

Preparation of M$_2$(NMe$_2$)$_5$(Ph$_3$Sn) (2). a. M = Mo. Neat Ph$_3$SnH (0.93 g, 2.65 mmol) was added dropwise with stirring to a solution of Mo$_2$(NMe$_2$)$_6$ (1.21 g, 2.65 mmol) dissolved in a minimum volume of chlorobenzene. After 45 min the mixture was filtered and the volume of the filtrate was reduced in vacuo. Orange-yellow Mo$_2$(NMe$_2$)$_5$(SnPh$_3$) (1.21 g, 60%) precipitated on standing at −40 °C for 16 h. Crystals suitable for analysis could only be obtained by slow cooling of saturated dimethoxyethane solutions. ^{1}H NMR (C$_6$D$_6$): 7.98–7.23 (m, 15, Ph), 4.19 (s, 6, NMe$_2$), 3.33 (s, 6, NMe$_2$), 3.26 (s, 12, NMe$_2$), 2.52 (s, 6, NMe$_2$). ^{13}C(^{1}H) NMR (C$_6$D$_6$): 149.0, 138.1, 127.5, 127.4 (s, Ph); 58.3, 50.7, 49.8, 41.6 (s, NMe$_2$). Anal. Calcd for Mo$_2$C$_{28}$H$_{45}$N$_5$Sn: C, 44.12; H, 5.95; N, 9.19. Found: C, 44.21; H, 5.94; N, 9.71.

b. M = W. A procedure similar to that in part a with W$_2$(NMe$_2$)$_6$ gave W$_2$(NMe$_2$)$_5$(SnPh$_3$) in a 50% yield.

Kinetic Measurements. Solutions of W$_2$(NMe$_2$)$_6$ and Ph$_3$SnH in 1 mL of toluene-*d*$_8$ were prepared at −40 °C. The amount of W$_2$(NMe$_2$)$_6$ was varied between 15 and 30 mg (0.024–0.048 mmol). Excesses, 10-, 15-, and 20-fold, of Ph$_3$SnH were used. ^{1}H NMR spectra of the samples were taken at −40 °C for background corrections. The samples were then warmed to 0 °C in an ice bath for periods of 15–30 min, between which they were cooled to −40 °C and their ^{1}H NMR spectra were recorded. The growth of the HNMe$_2$ signal was monitored against an internal standard of hexamethyldisiloxane.

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Doubly Charged Ion Mass Spectrometry of Metallocenes

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and T. F. Moran*

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A new type of mass spectrometry has been developed for analysis of organic compounds. This technique, termed doubly charged ion mass spectrometry,[1] is applied here to the examination of doubly charged ions produced by electron impact ionization of metallocenes M(Cp)$_2$ (M = Mn, Fe, Co, Ni; Cp is η^5-C$_5$H$_5$). Both singly and doubly charged ions are produced by electron impact ionization of neutral molecules; however, relatively little is known about doubly charged A^{2+} ions since their presence is obscured in many cases by singly charged (A/2)$^+$ ions apearing at the same mass-to-charge ratio. The purpose of this contribution is to illustrate how doubly charged ion mass spectrometry can be used to map the doubly charged ion domain exclusively and thereby obtain mass spectra as well as energies necessary to form doubly charged ions of inorganic compounds typified by the metallocenes.

Experimental Section

Doubly charged ion mass spectra have been obtained by using a double focusing Hitachi RMU-7L mass spectrometer of Nier–Johnson geometry. All singly and doubly charged ions produced by electron impact in the ion source are fully accelerated into the first field-free drift/collision region where doubly charged ions collide with target molecules T and readily undergo single-electron-transfer reactions of the type

$$\mathrm{M(Cp)_2^{2+}(fast) + T(slow) \rightarrow M(Cp)_2^{+}(fast) + T^{+}(slow)} \qquad (1)$$

Very little momentum is transferred in these reactions, and as a result the fast M(Cp)$_2^+$ product ions possess twice the kinetic energy of each singly charged ion formed in the ion source. These product ions are transmitted by the electrostatic energy analyzer operated at twice the normal voltage necessary to pass all other ions. The M(Cp)$_2^+$ ions emerging from the electrostatic sector next pass into the magnetic sector for momentum analysis. Fast product ions appear at a nominal mass m^* given by the mass-to-charge ratios [M(Cp)$_2^+$/e]^2/[M(Cp)$_2^{2+}$/2e], which unambiguously identifies both reactant and product ions of interaction 1.

Each metallocene under investigation served as both ion source gas and collision target gas. Pressures in the drift/collision region ranged from 5 × 10^{-6} to 1 × 10^{-5} torr. Mass spectrometer operating conditions: 80-V electron-accelerating voltage, 3.4-kV ion-accelerating voltage, and 240 °C ion source temperature. Absolute energy of the ionizing electron beam was confirmed with the aid of known ionization/appearance energies of doubly charged ions from reference standards[2] such as Ar (43.4 eV), N$_2$ (42.7 eV), and C$_6$H$_6$ (26.0 eV).

Metallocenes were prepared by procedures given by King.[3] All compounds were sublimed and stored until needed in evacuated ampules. Compounds, with the exception of stable ferrocene, were manipulated in an inert-gas atmosphere, and all were introduced into the mass spectrometer by means of the batch-inlet system.

Results and Discussion

Doubly charged ion mass spectra resulting from electron impact ionization of metallocene compounds are presented in Table I. This table lists masses of all product ions with relative intensities greater than 1% of that of the most intense ion in each spectrum. Ferrocene and cobaltocene spectra consist of a single intense peak resulting from reactions of molecular doubly charged Fe(Cp)$_2^{2+}$ and Co(Cp)$_2^{2+}$ ions, respectively. Molecular doubly charged ions are observed to be the only metal-containing species in Table I.

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