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] $M_2(O\text{-}t\text{-}Bu)_6$,[17] Ph_3SnH,[18] and Me_3SnH[18] were prepared by literature procedures. CP grade gases were used as received.

NMR shifts are reported in ppm referenced to Me_4Si for ^1H (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 ^1H-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_3SnH (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_2Cl_2/pentane. The resulting crystals lost solvent of crystallization on exposure to vacuum. ^1H NMR (C_6D_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 $MoC_{22}H_{27}N_2Sn$: C, 49.47; H, 5.10; N, 5.25. Found: C, 49.23; H, 5.20; N, 5.23.

Preparation of $M_2(NMe_2)_5(Ph_3Sn)$ (2). a. M = Mo. Neat Ph_3SnH (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. ^1H NMR (C_6D_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). $^{13}C\{^1H\}$ NMR (C_6D_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 $Mo_2C_{28}H_{45}N_5Sn$: 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_3SnH 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_3SnH were used. ^1H 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 ^1H NMR spectra were recorded. The growth of the $HNMe_2$ signal was monitored against an internal standard of hexamethyldisiloxane.

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[17] Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291–4293.

[18] van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. B. A. *J. Appl. Chem.* **1957**, *7*, 366.

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Doubly Charged Ion Mass Spectrometry of Metallocenes

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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_5H_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

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

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_6H_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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[1] Appling, J. R.; Musier, K. M.; Moran, T. F. *Org. Mass Spectrom.* **1984**, *19*, 412–422.

[2] Agee, J. H.; Wilcox, J. B.; Abbey, L. E.; Moran, T. F. *Chem. Phys.* **1981**, *61*, 171–179.

[3] King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1.

0020-1669/86/1325-1510$01.50/0

Table I. Doubly Charged Ion Mass Spectra and Appearance Energies (eV)[a] of Metallocene $M(Cp)_2$ Compounds

reactant ion	M = Co	M = Fe	M = Ni	M = Mn
$M(C_5H_5)_2^{2+}$	100.0 (21.1)	100.0 (22.7)	44.6 (22.5)	7.5 (21.4)
$C_{10}H_{10}^{2+}$				6.2
$C_{10}H_8^{2+}$			5.0	27.9 (23.4)
$C_{10}H_7^{2+}$				3.7
$C_{10}H_6^{2+}$				4.2
$C_8H_6^{2+}$				11.3 (26.1)
$C_5H_6^{2+}$			12.3	12.9
$C_5H_5^{2+}$			5.0	8.1
$C_5H_4^{2+}$			5.6	8.5
$C_5H_3^{2+}$			15.1	15.0
$C_5H_2^{2+}$			100.0 (25.2)	100.0 (30.7)
C_5H^{2+}			1.0	1.8
C_5^{2+}			1.2	

[a] The intensities of singly charged product ions of masses identical with those of the doubly charged reactant ions are listed first. Appearance energies for the respective ions are given in parentheses next to the ion intensities.

This is in contrast to conventional singly charged ion mass spectra[4] in which the most abundant metallocene fragment ions contain the constituent metal. Formation of $C_5H_2^{2+}$ rather than Ni^{2+} or Mn^{2+} in nickelocene and manganocene is consistent with charge localization on the separating fragment species that has the lower double ionization energy. The adiabatic ionization energy of C_5H_2 to form $C_5H_2^{2+}$ is 21.3 eV, which is 4.3 and 1.7 eV lower than the energies[5] required to form Ni^{2+} and Mn^{2+} ions. This adiabatic ionization energy is obtained from the difference in the heats of formation of geometry-optimized minimum-energy C_5H_2 and $C_5H_2^{2+}$ structures.[6]

Doubly charged ion mass spectra of manganocene and nickelocene are dispersed over a wide range with the most intense ion in each system being $C_5H_2^+$ from $C_5H_2^{2+}$ reactions. Product $C_5H_2^+$ ions have been found to be abundant in doubly charged ion mass spectra of hydrocarbons, and it has been suggested[6] that this is a consequence of the relatively low heat of formation of $C_5H_2^{2+}$ and its high barrier to dissociation. Likewise, product ions of the general formula $C_nH_6^+$ given in Table I are also prevalent[1] in doubly charged hydrocarbon ion spectra.

Neutral Mn and Ni metallocenes have higher multiplicities[7] than either Fe or Co complexes, and their ionic dissociation energies[9] are smaller than those for Fe or Co. It is not surprising that fragment ions comprise a greater percentage of the singly charged spectra of Mn and Ni as compared with the spectra of Fe and Co metallocenes. This same trend is observed for the doubly charged ion mass spectra shown in Table I where significant fragmentation occurs for Mn and Ni but not for Fe and Co metallocenes.

Energies to form the more abundant ions in doubly charged metallocene spectra are shown in parentheses in Table I. Variation of product ion intensity with ionizing electron energy is identical with that of its primary ion precursor formed in the ion source. The probability for forming doubly charged ions is a function of the square of the electron energy in excess of the ionization threshold; thus a plot of square root of ion intensity is a linear function of excess electron energy, and such a plot extrapolates to the ionization threshold for doubly charged ions.[2] Ionization energies so obtained for the metallocenes range from 21.1 eV required for formation of $Co(Cp)_2^{2+}$ to 22.7 eV for $Fe(Cp)_2^{2+}$. Energies required to remove two electrons from metallocene compounds are on the average 10% lower than second ionization energies[5] of the respective metal atoms. Similarly, the energies required to remove a single electron from these metallocenes are approximately 15% lower than the ionization energies of the corresponding gas-phase metal atoms. The development of intense doubly charged ion mass spectra for these compounds is not surprising in view of the relatively low electron energies required to form doubly charged ions. Extension of this technique to other systems is expected to provide similar information about the formation and energetics of doubly charged ions of other organometallic compounds.

Registry No. $Co(Cp)_2$, 1277-43-6; $Fe(Cp)_2$, 102-54-5; $Ni(Cp)_2$, 1271-28-9; $Mn(Cp)_2$, 73138-26-8.

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(4) Müller, J.; D'Or, L. *J. Organomet. Chem.* **1967**, *10*, 313–322.

(5) Moore, C. E. *Natl. Bur. Stand. Circ.* (*U.S.*) **1949**, No. 467.

(6) Burdick, G. W.; Shields, G. C.; Appling, J. R.; Moran, T. F. *Int. J. Mass Spectrom. Ion Processes* **1985**, *64*, 315–333.

(7) Molecular orbital designations of neutral Mn, Fe, Co, and Ni metallocenes: $(a_{1g})^1(e_{2g})^2(e_{1g}^*)^2$, $(a_{1g})^2(e_{2g})^4$, $(a_{1g})^2(e_{2g})^4(e_{1g}^*)^1$, $(a_{1g})^2(e_{2g})^4(e_{1g}^*)^2$, respectively.[8] Corresponding designations for singly charged ground-state ions:[8] $(a_{1g})^1(e_{2g})^2(e_{1g}^*)^1$, $(a_{1g})^2(e_{2g})^3$, $(a_{1g})^2(e_{2g})^4$, $(a_{1g})^2(e_{2g})^4(e_{1g}^*)^1$. Designations for doubly charged ions of these compounds: $(a_{1g})^1(e_{2g})^2$, $(a_{1g})^2(e_{2g})^2$, $(a_{1g})^2(e_{2g})^3$, $(a_{1g})^2(e_{2g})^4$.

(8) Cauletti, C.; Green, J. C.; Kelly, M. R.; Powell, P.; VanTilborg, J.; Robbins, J.; Smart, J. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327–353.

(9) Cais, M.; Lupin, M. S. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic: New York, 1970; pp 211–333.