the type described in Figure 6 (where L = CO) which conforms with the 18-electron rule and is derived from tetracobalt dodecacarbonyl by cleavage of one Co–Co bond with the concomitant formation of a Co–CO bond and a repositioning of one bridging carbon monoxide ligand. Indeed an intermediate of this configuration where $L = P(OCH_3)_3$ may well account for the interchange or associative term in these substitutional processes. The exchange reaction of $Co_4(CO)_{12}$ with the poor nucleophile ^{13}CO reported herein is believed not to be proceeding through this intermediate since the reaction was carried out at atmospheric CO pressure;[38] nevertheless, a more persuasive argument must await the determination of activation parameters for this CO-exchange process.

It appears that there is a need for much more kinetic data on substitutional processes in metal-cluster species before definitive statements regarding cooperativity between metal centers can be made. Clearly, studies should involve not only changes in metal centers but also variations in the steric and electronic nature of the substituent ligands. Work in progress includes kinetic measurements on ^{13}CO-exchange reactions with a variety of metal carbonyl cluster species, as well as phosphine and phosphite substitution processes with $Ir_4(CO)_{12}$ in hydrocarbon or other inert solvents.

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Note Added in Proof. We have completed recently X-ray structure determinations on two substituted cobalt species, $Co_4(CO)_{11}[P(C_6H_5)_3]$ and $Co_4(CO)_{10}[P(OCH_3)_3]_2$. The phosphine and phosphite ligands occupy axial coordination sites in these clusters.

Registry No. $Co_4(CO)_{11}[P(C_6H_5)_3]$, 12336-57-1; $Co_4(CO)_{10}[P(OCH_3)_3][P(C_6H_5)_3]$, 73953-20-5; $Co_4(CO)_{11}[P(OCH_3)_3]$, 56277-17-9; $Co_4(CO)_{12}$, 17786-31-1; $Co_4(CO)_{11}(^{13}CO)$, 73953-21-6; $Co_4(CO)_{10}(^{13}CO)_2$, 73953-21-6; $Co_4(CO)_9(^{13}CO)_3$, 73953-22-7; $Co_4(CO)_{10}[P(OCH_3)_3]_2$, 11067-01-9.

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[37] Bor, G.; Dietler, U. K.; Pino, P.; Poë, A. *J. Organomet. Chem.* **1978**, *154*, 301.

[38] The reaction studied in ref 37 involved CO pressures between 5 and 120 bar.

Contribution from the Department of Chemistry,
University College, Belfield, Dublin 4, Ireland

Reactions of Tin(II) Halides with Complexes Containing Two Transition Metal–Halogen Bonds, $[Co(\eta\text{-dienyl})(L)Y_2]$ and $[Fe(CO)_3(PPh_3)Y_2]$, and with $[Co(\eta\text{-dienyl})(CO)(C_3F_7)I]$ (Dienyl = C_5H_5 or MeC_5H_4; L = CO or PPh_3; Y = Br or I). A Novel Intramolecular Halogen Migration

JOHN FORTUNE and A. R. MANNING*

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Tin(II) halides, SnX_2 (X = Cl, Br, or I), react with an equimolar amount of $[Co(\eta\text{-dienyl})(CO)Y_2]$, $[Co(\eta\text{-dienyl})(PPh_3)Y_2]$, or $[Co(\eta\text{-dienyl})(CO)(C_3F_7)I]$ (dienyl = C_5H_5 or MeC_5H_4; Y = Br or I) in tetrahydrofuran solution at room temperature to give, in most instances, $[Co(\eta\text{-dienyl})(CO)(Y)(SnX_2Y)]$, $[Co(\eta\text{-dienyl})(PPh_3)(Y)(SnX_2Y)]$, or $[Co(\eta\text{-dienyl})(CO)(C_3F_7)(SnX_2I)]$. On the basis of the frequencies of the $\nu(CO)$ modes of the first series of compounds, it is concluded that during the $[Co(\eta\text{-dienyl})(CO)Br_2]/SnI_2$ reactions a novel halogen rearrangement occurs to give $[Co(\eta\text{-dienyl})(CO)(I)(SnBr_2I)]$ in which one of the less electronegative halogen atoms, I, migrates from tin to cobalt and both of the more electronegative bromine atoms migrate from cobalt to tin. $[Fe(CO)_3(PPh_3)Y_2]$ and SnX_2 generally give $[Fe(CO)_3(PPh_3)(Y)(SnX_2Y)]$, but when X = I and Y = Br, the only isolated product is $[Fe(CO)_3(PPh_3)I_2]$, and when Y = Br and X = Cl, some $[Fe(CO)_3(PPh_3)_2]$ is also formed. This last compound is the only product when an excess of triphenylphosphine is present, and the reaction is a rare example of a reductive elimination of a tin(IV) halide from a transition-metal complex. There is no evidence for the formation of SnX_3 derivatives or for complexes where SnX_2 inserts into both M–Y bonds under these conditions. It is suggested that a Lewis acid–Lewis base interaction between the SnX_2Y ligand and the Y ligand cis to it deactivates the second M–Y bond toward attack by tin(II) halides. A plausible reaction scheme is proposed which accounts for all of the above experimental observations.

Previously we showed that tin(II) halides, SnX_2 (X = Cl, Br, or I), reacted under mild conditions with a variety of compounds containing a single transition metal, M, to halogen, Y, bond, M–Y, to give $M{-}SnX_2Y$ derivatives as the initial products in most instances.[1,2] As a continuation of this work we have investigated the interaction of tin(II) halides with transition-metal complexes containing two halogen ligands. We anticipated that, as well as similarities between the two series of reactions, significant differences would be observed. This has proved to be the case. Our studies have been limited to the readily accessible derivatives of the first-row elements having the general formulas $[Fe(L)_nY_2]$ and $[Co(\eta\text{-dienyl})(L)Y_2]$ (L = CO, PPh_3, or CNMe; dienyl = C_5H_5 or MeC_5H_4; Y = Cl, Br, or I), but, recognizing the possibility of insertion into the $Co{-}C_3F_7$ bond, we also extended them to include $[Co(\eta\text{-dienyl})(CO)(C_3F_7)I]$.

Most of the previous work in this field has been devoted to the interaction of tin(II) chloride with the chlorides of the heavier metals and their coordination compounds. For example, Pregosin and Sze showed that various $[Pt(PR_3)_2Cl_2]$ and $SnCl_2$ react rapidly at room temperature to form $[Pt(PR_3)_2(Cl)(SnCl_3)]$ and then $[Pt(PR_3)_2(SnCl_3)_2]$.[3] However, of direct relevance to our work is that of Powell and Mays, who found that at room temperature in chloroform solution $[Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)I_2]$ and $SnCl_2$ gave only $[Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)(SnCl_3)_2]$.[4]

Experimental Section

Literature methods were used to synthesize $[Co(\eta\text{-}C_5H_5)(CO)_2]$[5] and $[Co(\eta\text{-}C_5H_5)(CO)Y_2]$ (Y = Br[6] or I[7]), their $(\eta\text{-}MeC_5H_4)$ counterparts,[5-7] $[Co(\eta\text{-}MeC_5H_4)(PPh_3)I_2]$,[7] $[Co(\eta\text{-}C_5H_5)\text{-}$

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[1] A. R. Manning, *Chem. Commun.*, 906 (1966).

[2] Bridget O'Dwyer and A. R. Manning, *Inorg. Chim. Acta*, **38**, 103 (1980), and references therein.

[3] P. S. Pregosin and S. N. Sze, *Helv. Chim. Acta*, **61**, 1848 (1978).

[4] E. W. Powell and M. J. Mays, *J. Organomet. Chem.*, **66**, 137 (1974).

[5] M. D. Rausch and R. A. Genetti, *J. Org. Chem.*, **35**, 3892 (1970).

[6] R. F. Heck, *Inorg. Chem.*, **4**, 855 (1965).

[7] R. B. King, *Inorg. Chem.*, **5**, 82 (1966).

0020-1669/80/1319-2590$01.00/0

Table I. Products from the Reactions Described in the Text and Their Decomposition Temperatures, Analyses, and IR Spectra

			anal., % [found (calcd)]					
Y	SnX_2Y^a	dec pt, °C	C	H	halogen	Co	Sn	IR spectra^b
$[Co(\eta\text{-}C_5H_5)(CO)(Y)(SnX_2Y)]$								
Br	$SnCl_2Br$	90	15.5 (14.3)	1.1 (0.9)	Br = 31.5 (31.8)			2071
Br	$SnBr_3$	140	12.3 (12.1)	0.9 (0.9)	Br = 53.9 (54.1)			2070
I	$SnBr_2I^c$	98	10.1 (10.5)	0.7 (0.7)		8.0 (8.6)	16.9 (17.3)	2058
I	$SnCl_2I$	87	11.7 (12.1)	1.2 (0.8)			18.6 (19.9)	2058
I	$SnBr_2I$	95	10.7 (10.5)	0.5 (0.7)	I = 36.9 (37.0)			2057
I	SnI_3	90	9.2 (9.3)	1.1 (0.7)	I = 64.8 (65.2)			2054
$[Co(\eta\text{-}MeC_5H_4)(CO)(Y)(SnX_2Y)]$								
Br	$SnCl_2Br^d$							2071
Br	$SnBr_3$	100	13.7 (13.8)	1.1 (1.4)	Br = 52.9 (52.9)	9.5 (9.7)		2070
I	$SnBr_2I^c$	107	12.2 (12.0)	0.9 (1.1)			14.3 (14.9)	2058
I	$SnCl_2I$	107	13.7 (13.7)	1.2 (1.3)	I = 41.6 (41.5)		19.0 (19.4)	2059
I	$SnBr_2I$	107	11.8 (12.0)	1.1 (1.1)	I = 36.7 (36.2)	7.0 (7.4)	16.7 (17.0)	2058
I	SnI_3	112	10.0 (10.5)	0.8 (1.0)	I = 63.3 (63.9)			2057
$[Co(\eta\text{-}MeC_5H_4)(PPh_3)(Y)(SnX_2Y)]$								
I	$SnCl_2I$	157	33.6 (34.1)	2.8 (2.6)	I = 29.7 (30.1)			
I	$SnBr_2I$	164	30.6 (30.8)	2.6 (2.3)	I = 27.7 (27.2)			
I	SnI_3		33.2 (28.0)	2.7 (2.1)	I = 49.8 (49.4)			
$[Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnX_2I)]$								
	$SnCl_2I$		16.9 (16.9)	1.0 (0.7)	I = 20.9 (20.8)	9.1 (9.2)		2077
	$SnBr_2I$		15.0 (14.9)	0.9 (0.6)	I = 16.9 (17.4)	7.1 (8.1)	16.0 (16.3)	2074
	$SnI_3{}^e$							2069
$[Fe(CO)_3(PPh_3)(Y)(SnX_2Y)]$								
Br	$SnCl_2Br$	130	32.9 (33.5)	1.9 (1.9)				2035 (4.8), 2050 (10), 2101 (1.2)
Br	$SnBr_3$		29.7 (29.9)	1.2 (1.7)	Br = 37.6 (38.0)			2035 (4.3), 2049 (10), 2101 (1.6)
I	I	135	39.1 (38.4)	2.7 (2.3)	I = 38.4 (38.7)			2023 (2.8), 2040 (10), 2089 (0.6)
I	$SnCl_2I$	121	29.6 (29.2)	2.2 (1.7)	I = 30.2 (30.7)			2023 (5.3), 2030 (10), 2079 (0.9)
I	$SnBr_2I$	130	26.4 (26.9)	1.7 (1.6)	I = 27.4 (27.1)			2022 (3.9), 2029 (10), 2079 (1.9)
I	SnI_3	95	23.1 (24.4)	1.1 (1.4)	I = 51.4 (49.3)			2022 (3.9), 2026 (10), 1079 (2.6)

[a] From the reactions of L_nMY_2 and SnX_2. [b] Frequencies (cm^{-1}) with relative intensities in parentheses for absorption bands due to the $\nu(CO)$ vibrations only. Measured in carbon disulfide solution. [c] Products from the $[Co(\eta\text{-dienyl})(CO)Br_2]/SnI_2$ reactions. [d] Not isolated but detected by IR spectroscopy. [e] Not isolated but detected by IR spectroscopy. It could be $[Co(\eta\text{-}C_5H_5)(CO)I_2]$. See text.

$(CO)(C_3F_7)I]$,[8] $[Fe(CO)_4I_2]$,[9] $[Fe(CO)_3(PPh_3)Y_2]$,[10] $[Fe(CO)_2(PPh_3)_2Y_2]$,[10] $[Fe(CO)_2(CNMe)_2Y_2]$,[11] $SnBr_2$,[12] and SnI_2.[12] Other chemicals were purchased. Solvents were purified by refluxing over calcium hydride (for benzene, dichloromethane, ether, hexane, and tetrahydrofuran) or magnesium (for methanol) under an atmosphere of nitrogen and distilled before use.

All reactions were carried out in the dark under an atmosphere of nitrogen at room temperature by using the same general procedure unless it is stated otherwise. Equimolar amounts of the transition-metal complex (1 g) and tin(II) halide were dissolved in tetrahydrofuran (50 mL) and the mixture was stirred until IR spectroscopy or changes in color showed the reactions to be complete. This was less than 5 min in most instances. The solutions were filtered, the solvents removed at reduced pressure, and the residues recrystallized from dichloromethane–hexane mixtures. (Recrystallization was the only mode of product purification open to us. Complexes containing the trihalotin ligands usually react irreversibly with silica or alumina in chromatography columns.) As we considered product purity to be of prime importance, no attempts were made to maximize product yields which were usually ca. 50% except in the case of the $[Co(\eta\text{-dienyl})(CO)Br_2]/SnX_2$ reactions where they were 30%. However there was no evidence for reaction products other than those described in the Results and Discussion. Also, it should be noted that unless the tin(II) halides were dissolved in tetrahydrofuran before $[Fe(CO)_3(PPh_3)Y_2]$, these reactions gave no isolable products, only intractable precipitates.

The reaction products are listed in Table I together with their decomposition points, analyses, and IR spectra in the 1700–2100-cm^{-1} region. The analyses were carried out in the Analytical Laboratory, University College Dublin, and the IR spectra were obtained as described elsewhere.[2]

Results and Discussion

The reactions of equimolar amounts of $[Co(\eta\text{-dienyl})(L)Y_2]$ and SnX_2 (dienyl = C_5H_5 or MeC_5H_4; L = CO or PPh_3; X = Cl, Br, or I; Y = Br or I) at room temperature in the dark usually gave 1:1 adducts having the formula $[Co(\eta\text{-dienyl})(L)SnX_2Y_2]$. They were complete in 5–10 min in tetrahydrofuran solution but did not appear to take place in benzene, ether, or methanol solutions. The products were brown (L = CO) or dark red (L = PPh_3), air-stable, crystalline solids which did not melt on heating but decomposed (Table I). Their solutions in common organic solvents decomposed slowly.

The reactions were not always successful. Although $[Co(\eta\text{-}MeC_5H_4)(CO)Br_2]$ and $SnCl_2$ reacted completely to give a 1:1 adduct which could be identified by IR spectroscopy, we could not isolate it. Also, the $[Co(\eta\text{-}MeC_5H_4)(PPh_3)I_2]/SnI_2$ reaction only went to completion with an excess (ca. 3 mol) of tin(II) iodide. The $[Co(\eta\text{-}MeC_5H_4)(PPh_3)SnI_4]$ thus formed was unstable and reverted in part to $[Co(\eta\text{-}MeC_5H_4)(PPh_3)I_2]$ on attempted purification.

In no reaction that we investigated during the course of this work did we observe the formation of 1:2 adducts of the type $[Co(\eta\text{-dienyl})(L)Sn_2X_4Y_2]$ (or $[Fe(CO)_3(PPh_3)Sn_2X_4Y_2]$) when the reactant mole ratio was 1:1. If an excess of SnX_2 was added to a solution of $[Co(\eta\text{-}C_5H_5)(CO)I_2]$, only $[Co(\eta\text{-}C_5H_5)(CO)SnX_2I_2]$ could be isolated even after 2 h, but with $[Co(\eta\text{-}C_5H_5)(CO)Br_2]$ a slow, complicated reaction took place which we are attempting to unravel. Also, we did not encounter halogen-exchanged products of the type $[Co(\eta\text{-dienyl})(L)SnX_4]$. These results contrast with the preparation of $[Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)(SnCl_3)_2]$ from $[Co(\eta\text{-}C_5H_5)(CNC_6H_4OMe\text{-}p)I_2]$, but here larger quantities of tin(II) chloride were used (ca. 6 mol) together with longer re-

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(8) R. B. King, P. M. Treichel and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).
(9) W. Hieber and G. Bader, *Ber. Dtsch. Chem. Ges.*, **61**, 1717 (1928).
(10) W. Hieber and J. Muschi, *Chem. Ber.*, **98**, 3931 (1965).
(11) R. C. Taylor and W. D. Horrocks, Jr., *Inorg. Chem.*, **3**, 584 (1964).
(12) C. C. Hsu and R. A. Geanangel, *Inorg. Chem.*, **16**, 2529 (1977).

action times and chloroform solvent.[4]

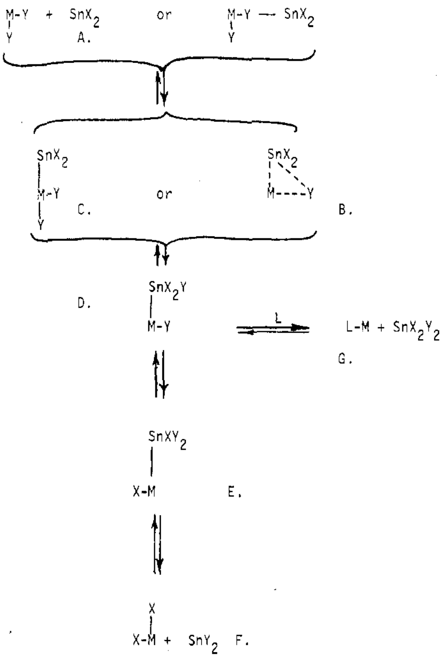
The compounds we have prepared are of the same type as the $[Co(\eta-C_5H_5)(CO)(X)(SnX_3)]$ derivatives obtained by Kummer and Graham from the oxidative addition of SnX_4 to $[Co(\eta-C_5H_5)(CO)_2]$.[13] Most arise from the insertion of SnX_2 into one Co–Y bond, i.e., are formulated as $[Co(\eta\text{-dienyl})(L)(Y)(SnX_2Y)]$. However this is not always the case, and in some reactions only $[Co(\eta\text{-dienyl})(L)(X)(SnXY_2)]$ are formed.

These two possible isomers may be distinguished readily when L = CO by their IR spectra in the 1700–2100-cm^{-1} region. For all such compounds single absorption bands are observed due to their single $\nu(CO)$ vibrations, their frequency being lower for $[Co(\eta\text{-dienyl})(CO)(Y)(SnX_2Y)]$ than for $[Co(\eta\text{-dienyl})(CO)Y_2]$. The frequency is not affected to any great extent by the halogen atoms bonded to tin although it does decline by ca. 2–4 cm^{-1} as these increase in atomic number in going from $SnCl_2I$ to SnI_3. On the other hand, it is affected markedly by the halogen atom bonded to cobalt and declines by ca. 12 cm^{-1} as this changes from bromine to iodine. Thus it is possible to state unambiguously that the products from the reactions of $[Co(\eta\text{-dienyl})(CO)Br_2]$ with SnI_2 are not $[Co(\eta\text{-dienyl})(Br)(SnI_2Br)]$ with a Co–Br bond for which one would anticipate $\nu(CO) \approx 2070$ cm^{-1}. Instead they are better formulated as $[Co(\eta\text{-dienyl})(CO)(I)(SnBr_2I)]$ with a Co–I bond for which $\nu(CO) \approx 2058$ cm^{-1} is expected and has been observed (Table I). During the course of the reaction, rearrangement has occurred so that the more electronegative halogen has migrated from cobalt to tin. This type of reaction has not been reported previously to the best of our knowledge and leads one to expect that if it were possible to prepare $[Co(\eta\text{-dienyl})(CO)Cl_2]$ and study their reactions with SnX_2 (X = Br or I), the products would be $[Co(\eta\text{-dienyl})(CO)(X)(SnCl_2X)]$ rather than the direct-insertion products $[Co(\eta\text{-dienyl})(CO)(Cl)(SnX_2Cl)]$.

The reaction of $[Co(\eta-C_5H_5)(CO)(C_3F_7)I]$ with SnX_2 gave red crystalline 1:1 adducts when X = Cl or Br. When X = I, the reaction was not complete and the product could not be isolated although it gave rise to a $\nu(CO)$ absorption band at 2069 cm^{-1}. In many respects the C_3F_7 group may be regarded as a pseudohalogen and the tin(II) halide could insert into the Co–C_3F_7 or Co–I bonds. A comparison of the frequencies of the $\nu(CO)$ absorption bands of the relevant (η-cyclopentadienyl)cobalt complexes (Table I) suggests that the overall electron-withdrawing ability of the perfluoropropyl group, C_3F_7, is somewhat greater than that of the bromo ligand and that the adducts where X = Cl or Br are best formulated as $[Co(\eta-C_5H_5)(CO)(C_3F_7)(SnX_2I)]$ arising from SnX_2 insertion into the Co–I bond. When X = I, the incompletely formed product may be of this type, but equally it may be $[Co(\eta-C_5H_5)(CO)I_2]$. It is very unlikely to be $[Co(\eta-C_5H_5)(CO)(I)(SnI_2C_3F_7)]$. Our data do not allow the two alternatives to be distinguished unambiguously.

The other series of SnX_2 insertion reactions that we investigated were those with complexes of iron(II) halides. In our hands $[Fe(CO)_2(CNMe)_2Y_2]$ and $[Fe(CO)_2(PPh_3)_2Y_2]$ failed to react at room temperature in tetrahydrofuran solution, and $[Fe(CO)_4Y_2]$ (Y = Br or I) were unstable in solvents which dissolved tin(II) halides so we did not pursue the problem. However, $[Fe(CO)_3(PPh_3)Y_2]$ derivatives (Y = Br or I) and SnX_2 (X = Cl or Br) usually formed 1:1 adducts as air-stable, red crystalline solids, but a persistent byproduct from the $[Fe(CO)_3(PPh_3)Br_2]/SnCl_2$ reaction was $[Fe(CO)_3(PPh_3)_2]$. If 1 mol or more of triphenylphosphine was added to the reaction mixture, this compound became the sole product.

Scheme I. Proposed Scheme for Reaction of SnX_2 with $[Co(\eta\text{-dienyl})(L)Y_2]$ and $[Fe(CO)_3(PPh_3)Y_2]$ Derivatives[a]



[a] MY_2 = $[Co(\eta\text{-dienyl})(L)Y_2]$ or $[Fe(CO)_3(PPh_3)Y_2]$ (ligands other than halogens Y have been omitted for the sake of clarity). L = PPh_3.

On the other hand, SnI_2 and $[Fe(CO)_3(PPh_3)Br_2]$ gave $[Fe(CO)_3(PPh_3)I_2]$ as the only isolable product, while the $[Fe(CO)_3(PPh_3)I_2]/SnI_2$ reaction did not go to completion unless an excess of stannous iodide was present. An analytically pure sample of the product could not be obtained, but it could be identified by IR spectroscopy.

The 1:1 adducts are formulated as $[Fe(CO)_3(PPh_3)(Y)(SnX_2Y)]$ derivatives arising from the insertion of SnX_2 into one Fe–Y bond. Kummer and Graham have prepared similar complexes with Y = X by the oxidative addition of SnX_4 to $[Fe(CO)_4(PPh_3)]$ or $[Fe(CO)_3(PPh_3)_2]$.[14] The IR spectra of the compounds in the 1700–2100-cm^{-1} region are consistent with a cis arrangement of the Y and SnX_2Y ligands in an octahedral complex and with PPh_3 trans to one of them.[14] It should be noted that the frequencies of the three $\nu(CO)$ modes of these derivatives (Table I) are higher by ca. 20–30 cm^{-1} when the halogen bonded to iron is Br rather than I, but they are not greatly affected by variations of the halogen atoms bonded to tin. These frequency variations allow one to state unambiguously that halogen transfer from tin to iron does not occur except in the reaction of $[Fe(CO)_3(PPh_3)Br_2]$ and SnI_2. Our studies on the $[Co(\eta\text{-dienyl})(CO)Y_2]/SnX_2$ reactions would lead us to expect this result, but unfortunately we were not able to isolate the tin-containing complex $[Fe(CO)_3(PPh_3)(I)(SnBr_2I)]$ which could be a precursor to the isolated $[Fe(CO)_3(PPh_3)I_2]$.

There is no evidence for the formation of products containing the SnX_3 group in the reactions of equimolar amounts of SnX_2 and the iron or cobalt complexes containing two metal–halogen bonds when these are carried out under mild conditions. This observation eliminates the possibility that Y^- is displaced by SnX_3^-, or by X^-, prior to SnX_2 insertion. We had previously suggested a mechanism for the insertion of SnX_2 into a single M–Y bond in ref 1 which accounts for this observation. It has been expanded and refined in ref 2, and it is applicable in the present instance. It is shown by A → D in Scheme I,

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[13] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 7, 523 (1968).

[14] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, 7, 1209 (1968).

but we are not able to determine if it proceeds via a three-center transition state such as B or an intermediate with a M–SnX_2 bond such as C. The halogen interchange with the migration of the least electronegative halogen from Sn to the transition metal M takes place by a similar series of reactions, which are not illustrated in detail, in D → E. The extrusion of SnY_2 from E, the reverse of A → D, which results only in halogen exchange at M, is E → F although again the individual steps are not illustrated. The reaction D → G which takes place for M = $Fe(CO)_3(PPh_3)$ in the presence of excess L = PPh_3 is the reverse of Kummer and Graham's oxidative addition of tin(IV) halides to $[Fe(CO)_3(PPh_3)_2]$. It provides a rare example of the reductive elimination of tin(IV) halides from a transition-metal complex (we have not been able to trace another), whereas the reverse is well-known.

All of the various steps in Scheme I are probably reversible (cf. ref 15). Together they constitute a series of equilibria, the positions of which vary with metal, halogen, other ligands, and reaction conditions. It is possible that the halogen interchange (D → E) may take place by complete dissociation of SnXY from D followed by its attack on the M–Y bond of the residual M(X)Y moiety. Our inability to detect $M(SnX_3)Y$ species tends to weigh against such a suggestion but does not rule it out.

The absence of $M(SnX_2Y)_2$ derivatives from our reaction mixtures when equimolar amounts of the reactants are used is a clear indication that the SnX_2Y ligand deactivates the second M–Y bond toward SnX_2 insertion. This may be for steric reasons, but it may also be a consequence of the Lewis acid nature of the SnX_2Y ligand[16] and the presence of a Lewis acid–Lewis base interaction between it and Y ligand which is always cis to it in our complexes. Such an interaction would account also for the facile loss of $SnCl_2Br_2$ from $[Fe(CO)_3(PPh_3)(Br)(SnCl_2Br)]$ in the presence of excess PPh_3.

Registry No. $Co(\eta\text{-}C_5H_5)(CO)Br(SnCl_2Br)$, 74007-65-1; $Co(\eta\text{-}C_5H_5)(CO)Br(SnBr_3)$, 12305-13-4; $Co(\eta\text{-}C_5H_5)(CO)I(SnBr_2I)$, 74007-66-2; $Co(\eta\text{-}C_5H_5)(CO)I(SnCl_2I)$, 74007-67-3; $Co(\eta\text{-}C_5H_5)(CO)I(SnI_3)$, 12305-20-3; $Co(\eta\text{-}MeC_5H_4)(CO)Br(SnCl_2Br)$, 74019-24-2; $Co(\eta\text{-}MeC_5H_4)(CO)Br(SnBr_3)$, 74019-25-3; $Co(\eta\text{-}MeC_5H_4)(CO)I(SnBr_2I)$, 74019-26-4; $Co(\eta\text{-}MeC_5H_4)(CO)I(SnCl_2I)$, 74019-27-5; $Co(\eta\text{-}MeC_5H_4)(CO)I(SnI_3)$, 74019-28-6; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I(SnCl_2I)$, 74019-29-7; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I(SnBr_2I)$, 74019-30-0; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I(SnI_3)$, 74019-31-1; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnCl_2I)$, 74007-68-4; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnBr_2I)$, 74007-69-5; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)(SnI_3)$, 74007-70-8; $Fe(CO)_3(PPh_3)Br(SnCl_2Br)$, 74007-71-9; $Fe(CO)_3(PPh_3)Br(SnBr_3)$, 41333-06-6; $Fe(CO)_3(PPh_3)I(SnCl_2I)$, 74007-72-0; $Fe(CO)_3(PPh_3)I(SnBr_2I)$, 74007-73-1; $Fe(CO)_3(PPh_3)I(SnI_3)$, 19601-48-0; $Co(\eta\text{-}C_5H_5)(CO)Br_2$, 12144-83-1; $Co(\eta\text{-}C_5H_5)(CO)I_2$, 12012-77-0; $Co(\eta\text{-}MeC_5H_4)(CO)Br_2$, 74007-74-2; $Co(\eta\text{-}MeC_5H_4)(CO)I_2$, 74007-75-3; $Co(\eta\text{-}MeC_5H_4)(PPh_3)I_2$, 74007-76-4; $Co(\eta\text{-}C_5H_5)(CO)(C_3F_7)I$, 12128-52-8; $Fe(CO)_3(PPh_3)Br_2$, 15388-83-7; $Fe(CO)_3(PPh_3)I_2$, 51744-71-9; $SnBr_2$, 10031-24-0; SnI_2, 10294-70-9; $SnCl_2$, 7772-99-8.

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Contribution from the Department of Chemistry,
University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Alkylation and Ligand Substitution Reactions of Binuclear Organosulfur Molybdenum Complexes with Phosphites and Phosphines

JUDITH HARTGERINK, NED D. SILAVWE, and HOWARD ALPER*[1]

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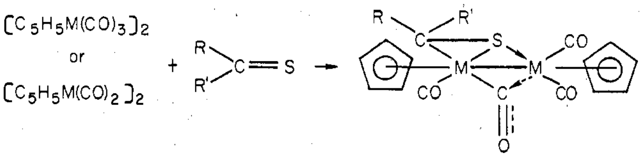
Binuclear organosulfur molybdenum complexes, of formula $(C_5H_5)_2Mo_2(CO)_4(R_2CS)$, which contain a metallathiacyclopropane unit and a semibridging carbonyl group, react with phosphites and alkoxyphosphines to give alkyl migration and ligand substitution products. The alkylated products are of lateral stereochemistry. Mechanisms are proposed for these reactions.

The reaction of thioketones with dicyclopentadienylhexacarbonyl- or dicyclopentadienyltetracarbonyldimolybdenum or -ditungsten results in the formation of complexes of structural type **1** (see Scheme I). These complexes contain a metallathiacyclopropane unit as well as a semibridging carbonyl group.[2] We anticipated that these novel organosulfur complexes would exhibit interesting chemical behavior. For example, would reactions occur which would result in retention or cleavage of the semibridging carbonyl group, metal–metal bond, or the metallathiacyclopropane unit? We now report the results of an investigation of the reactions of organomolybdenum complexes with phosphites and phosphines.

Results and Discussion

Treatment of the binuclear complex **2**, R = OCH_3, with triethyl phosphite in benzene at 60 °C for 15 h affords the mononuclear complex **3**, R = OCH_3, R′ = C_2H_5, in 92% yield (see Scheme II). The yields, melting points, and analytical data for **3** and for the other products of the phosphite and phosphine reactions are given in Table I. Pertinent infrared, magnetic resonance (^1H, ^{13}C, ^{31}P), and mass spectral data are listed in Table II.

Scheme I



1

M = Mo, W

Complex **3**, R = OCH_3, R′ = C_2H_5, has several very interesting structural features. One can consider **3** to be square pyramidal in geometry, if it is assumed that the thiocarbonyl group occupies one coordination site. In that event, two stereoisomers are possible, a lateral (also denoted as cis) and a diagonal (trans).[3-5] The spectral data indicate that the

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