We intend to extend the strategy presented here with other ligands and metals.

Acknowledgment. We are greatly indebted to Professors Didier Astruc, John E. Bercaw, and Clifford A. Bunton for helpful discussions and miscellaneous analysis. We also with to thank Barbara J. Burger for her help in the preparation of this manuscript.

Registry No. **1**, 14024-17-0; **2**, 97210-26-9; **3**, 97210-27-0; **4**, 52409-66-2; **5**, 76747-93-8; **6**, 97210-28-1; **7**, 97210-29-2; **8**, 97210-30-5; **9**, 97210-31-6; **10**, 83928-47-6; **11**, 97210-32-7; **12**, 75730-73-3; **13**, 97190-28-8; **14**, 97190-29-9; **15**, 97210-33-8; **16**, 97210-34-9; C_5Me_5Li, 51905-34-1; MeI, 74-88-4; $Co(acac)_2$, 14024-48-7; $Ni(acac)_2$, 3264-82-2; C_5H_5Na, 4984-82-1; p-$C_6H_4Br_2$, 106-37-6; 3,4-dimethylcyclopent-2-en-1-one, 30434-64-1; 2,3,4,5-tetramethylcyclopent-2-en-1-one, 54458-61-6.

Thallium(I)-Promoted Substitution Reactions of Chloromethyl Complexes of Iron and Molybdenum with Uncharged Nucleophiles

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Summary: $TlBF_4$ has been used as an electrophilic promotor for substitution of chloride in $[Fe(\eta^5\text{-}C_5H_5\text{-}(CO)_2CH_2Cl]$ and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3CH_2Cl]$ by a wide range of uncharged nucleophiles. The resulting fluoroborate onium salts are obtained in high yield.

Nucleophilic substitution of halide in halomethyl complexes L_nMCH_2X would appear to be an attractive approach to the preparation of a variety of other alkyl complexes. Indeed, a number of successful substitution reactions of such compounds have been reported.[1] However, some attempts to substitute the halide in certain halomethyl complexes by neutral nucleophiles have met with only limited success. In particular, Moss and co-workers report very erratic results in reactions of various phosphines with $[FeCp(CO)_2CH_2Cl]$ (A) and that some compounds, including $[MoCp(CO)_3CH_2Cl]$ (B) ($Cp = \eta^5\text{-}C_5H_5$), fail to give any halide substitution product at all.[1g] Attempts in our laboratory to substitute A with either $HNEt_2$ or NEt_3 were unsuccessful.[2] We now wish to report that $TlBF_4$ can be used to promote halide substitution by a variety of neutral nucleophiles in both A and B to give the onium salts in excellent yield.

A list of the compounds prepared by the thallium promoted method with yields and spectroscopic data are given in Table I. All of the compounds were prepared by stirring a suspension of 1.2–2 equiv of $TlBF_4$ in a methylene chloride solution of A[1f] or B[3] (3–5 mmol in 25 mL) and 1–5 equiv of nucleophile at room temperature.[4,5] Reactions of A were complete in 5–20 h whereas B reacted much more slowly, and 2–4 days were required to achieve conversions of 50–60%. It is important to note that there is no evidence for loss of B to other reactions and that greater conversions can likely be achieved with longer reaction times. Attempts to perform reactions of B at higher temperature resulted in the formation of other products.[6] Workup involved filtration to remove thallium salts, concentration, and addition of hexane to crystallize the products.[7] Characterization of the new compounds in Table I on the basis of IR and NMR spectral data and elemental analyses[8] was straight forward.

Of the compounds listed in the table only **1** and some of its analogues have been previously prepared by direct reaction of A with the phosphines.[1g] The other known complexes **5**[9a] and **6**[9b] were prepared by an alternative route, as was the methyl analogue of **2**.[10] We believe that the thallium(I)-promoted reaction is superior to these methods.

In principle, it should be possible to perform anion substitution reactions with thallium salts whose solubility is comparable or greater than that of thallium chloride. We have observed that A reacts rapidly with TlOEt and more slowly with the less soluble TlOAc. Infrared spectra of the reaction mixtures indicate that $[FeCp(CO)_2CH_2OEt]$[1f] and $[FeCp(CO)_2CH_2OC(O)CH_3]$[1f] are the only detectable carbonyl containing species present.

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(1) Substitution in $[FeCp(CO)_2CH_2X]$: (a) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926. (b) Jensen, J. E.; Campbell, L. L.; Nakanishi, S.; Flood, T. C. *J. Organomet. Chem.* **1983**, *244*, 61. (c) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910. (d) Flood, T. C.; DiSanti, F. J.; Miles, D. L. *J. Chem. Soc., Chem. Commun.* **1975**, 336. (e) Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7. (f) Green, M. L. H.; Ishaq, M.; Whiteley, R. N. *J. Chem. Soc. A* **1967**, 1508. Substitutions in $[FeCp(CO)_2CH_2Cl]$ and $[WCp(CO)_3CH_2Cl]$ and attempted substitution in $[MoCp(CO)_3CH_2Cl]$, $[RuCp(CO)_2CH_2Cl]$, and $[M(CO)_5CH_2Cl]$ (M = Mn, Re): (g) Pelling, S.; Botha, C.; Moss, J. R. *J. Chem. Soc., Dalton Trans.* **1983**, 1495. Substitutions in $[PtL_2(CH_2X)(X)]$ (L = tertiary phosphine): (h) Engelter, C.; Moss, J. R.; Niven, M. L.; Nassimbeni, L. R.; Reid, G. *J. Organomet. Chem.* **1982**, *232*, C78. (i) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Organomet. Chem.* **1982**, *228*, C71. (j) Kermode, N. J.; Lappert, M. F.; Skelton, B. W.; White, A. H.; Holton, J. *J. Chem. Soc., Chem. Commun.* **1981**, 698. (k) Scherer, O. J.; Jungmann, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1663. Substitutions in $[RhCp(L)_2CH_2I]^+$ (L = tertiary phosphine) and $[RhCp(PMe_3)(CH_2I)(I)]$: (l) Paul, W.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 316. (m) Werner, H.; Hofmann, L.; Paul, W. *J. Organomet. Chem.* **1982**, *236*, C65. (n) Werner, H.; Feser, R.; Paul, W.; Hofmann, L. *J. Organomet. Chem.* **1981**, *219*, C29. (o) Feser, R.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 940. Reduction of $[Os(CH_2I)I(CO)_2(PPh_3)_2]$ by BH_4^-: (p) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7. α-Halide exchange in a number of perfluoroalkyls: (q) Richmond, T. G.; Shriver, D. F. *Organometallics* **1984**, *3*, 305.

(2) Attempts were made by using both $HNEt_2$ or NEt_3 in THF with and without added $AgBF_4$. Sepelak, D. J.; Barefield, E. K., unpublished results.

(3) King, R. B.; Braitsch, D. M. *J. Organomet. Chem.* **1973**, *54*, 9.

(4) Reactions of A with Me_2S and PMe_2Ph were attempted without addition of $TlBF_4$. After 16 h the dimethyl sulfide reaction mixture was completely homogeneous and A was the only detectable (infrared and ^1H NMR spectra) iron carbonyl product. After 16 h the PMe_2Ph reaction contained a white precipitate that was identified as $[PhPMe_3]Cl$ based on its ^1H NMR spectrum (Knoll, L. *J. Organomet. Chem.* **1979**, *182*, 77). Most of the A had reacted to give a monocarbonyl species which was probably $[FeCp(CO)(PMe_2Ph)_2]^+$ [ν_{CO} 1966 cm^{-1} (lit.,[1g] ν_{CO} 1967 cm^{-1})]. A small amount of starting material remained. There was no evidence for the presence of **1**.

(5) Complexes A and B do not react with $TlBF_4$ in CH_2Cl_2 in the absence of nucleophile. Complex A does however react with $TlBF_4$ in Me_2SO, CH_3CN, and THF. The products of these reactions have not been characterized.

(6) No attempts were made to separate the product mixtures, but the infrared and ^1H NMR spectra suggested that CO substitution products were formed when reaction mixtures containing NEt_3 and PMe_2Ph were heated.

(7) $\{FeCp(CO)_2[CH_2P(OMe)_3]\}BF_4$ has a melting point below room temperature. It separated as a viscous oil upon addition of hexane to the CH_2Cl_2 solution.

(8) All products in Table I gave satisfactory elemental analyses.

(9) (a) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869. (b) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473.

(10) Barefield, E. K.; Sepelak, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6542.

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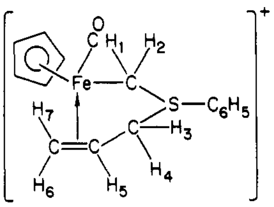
Table I. Compounds Prepared from Complexes A and B by $TlBF_4$-Promoted Substitution Reactions

				^1H NMR chem shifts, δ (J, Hz)[d]		
complex	yield, %	mp,[a] °C	ν_{CO},[c] cm^{-1}	η^5-C_5H_5	MCH_2	other
$[FeCp(CO)_2CH_2X]BF_4$						
1, X = $P(CH_3)_2Ph$	97	89–98 dec	2018, 1976	4.89	2.12 (d, J_{PH} = 14)	CH_3, 1.83 (d, J_{PH} = 12); Ph, 7.08–7.83 (m)
2, X = $N(CH_2CH_3)_3$	90	126–130 dec	2021, 1971	5.05	3.63	CH_3, 1.23 (t, J = 7); CH_2, 3.03 (q)
3, X = NC_5H_5	81	126–128 dec	2028, 1979	5.21	4.94	*m*-H, 7.95 (t, J = 7); *p*-H, 8.32 (t, J = 7); *o*-H, 8.98 (d, J = 7)
4, X = $P(OCH_3)_3$	90	*b*	2030, 1985	5.26	0.98 (d, J_{PH} = 12)	CH_3, 4.08 (d, J_{PH} = 11)
5, X = $S(CH_3)_2$	80	127–136 dec	2024, 1975	5.33	2.73	CH_3, 3.00
6, X = $S(CH_3)Ph$	100	97–102 dec	2030, 1985	5.37	2.97 (d), 3.23 (d, J = 10)	*m*, *p*-H, 7.72–7.96 (cm); *o*-H, 8.03–8.21 (m)
7, X = SPh_2	100	113–168 dec	2034, 1990	5.31	3.53	*m*,*p*-H, 7.52–7.75 (m); *o*-H, 7.93–8.17 (m)
8, X = $S(C_3H_5)Ph$	98	115–117 dec	2032, 1988	5.27	3.27 (d), 2.88 (d, J = 10)	SCH_2, 4.36 (q of d, J_{AB} = 12, $\Delta\nu$ = 47, J_{AX} = J_{BX} = 8); $=CH_2$, 5.26–5.38 (m); CH=, 5.68–5.86 (m); *m*,*p*-H, 7.69–7.83 (m); *o*-H, 8.07–8.11 (m)
$[MoCp(CO)_3CH_2X]BF_4$						
9, X = NC_5H_5	72	137–138 dec	2036, 1945	5.89	5.26	*m*-H, 8.05 (m); *p*-H, 8.42 (t, J = 8); *o*-H, 9.01 (d, J = 6)
11, X = $S(CH_3)_2$	61	116–118 dec	2040, 1955	5.86	2.88	CH_3, 3.03
12, X = $S(CH_3)Ph$	61	109–112 dec	2042, 1968	5.80	3.26 (q, J_{AB} = 11, $\Delta\nu$ = 33)	SCH_3, 3.37; *m*,*p*-H, 7.73–7.84 (m); *o*-H, 8.12–8.14 (m)

[a] Uncorrected. [b] See ref 7. [c] CH_2Cl_2. [d] 300 MHz, acetone-d_6/Me_4Si standard.

Silver ion is a much more commonly utilized halophile for promoting substitution reactions.[11] Although we have not attempted to use silver salts as an alternative to thallium in all of the above reactions, we have been markedly unsuccessful with amines[2] apparently because of the substantial stability of the silver complexes of these ligands. Thallium has the distinct advantage over silver of forming few complexes,[12] and it is a much weaker oxidizing agent.[13] Unlike silver(I), thallium(I) did not react with A in methylene chloride except in the presence of the nucleophile.

Preliminary investigations on some of the new compounds indicate that they have very interesting chemical properties. For example, photolysis of 8 (Hg lamp, CH_2Cl_2 solution, 22 °C) results in quantitative conversion to a 1.5–1.8:1 ratio of two of the four possible diastereoisomers of **13**.[14–16] Thermolysis of the mixture of stereoisomers in refluxing dichloroethane resulted in a 85% yield of a mixture of 4-butenyl phenyl sulfide[17] and 2-methyl-2-propenyl phenyl sulfide[18] (ca. 9:1 ratio). Thermolysis of 8 under the same conditions did not produce either sulfide. A mechanistic study of the homologation reaction is in progress.



13

Recently sulfonium salts 5[9a] and 6[9b] have been shown to be useful as methylene-transfer reagents for cyclopropanation of olefins with 6 being considerably more reactive than 5. Diphenyl analogue 7 might be expected to be even more reactive, but it had not been previously possible to synthesize it. Preliminary studies suggest that this is indeed the case since greater than 85% yields of bicyclo[6.1.0]nonane can be obtained from 1:1 ratios of 7 and cyclooctene after 3-h reaction time at 22 °C. A mechanistic study of this reaction, to be reported separately, indicates that it proceeds by a dissociative process.

We anticipate that other (halomethyl)metal complexes will also undergo thallium(I)-promoted substitution reactions. The results reported here clearly indicate that a wide range of nucleophiles, including some very weak ones, can be employed and that new complexes with interesting reactivities can be prepared.

Registry No. **1**, 97374-89-5; **2**, 97374-91-9; **3**, 97374-93-1; **4**, 97374-95-3; **5**, 72120-26-4; **6**, 97374-97-5; **7**, 97374-99-7; **8**,

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(11) $AgPF_6$ was used by Brandt and Cutler to promote substitution of chloride by CO in $[CpFe(CO)_2CH_2Cl]$.[1a] Silver salts have been used in at least two instances to promote electrophilic attack of $[CpFe(CO)_2CH_2Cl]$ on unsaturated species, i.e., cyclopropanation of olefins: Jolly, P. W.; Pettit, R. *J. Am. Chem. Soc.* **1966**, *88*, 5044. Conversion of $[Pt(PPh_3)_2(CH_2X)(X)]$ to $[\overline{PtCH_2C_6H_4P}Ph_2(PPh_3)(solvent)]^+$ (2 equiv of Ag^+ required): Yang, Z.-Y.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1984**, 2019.

(12) Lee, A. G. "The Chemistry of Thallium"; Elsevier: New York, 1971.

(13) Standard electrode potentials in aqueous solution are Ag^+/Ag, 0.8 V, Tl^+/Tl, –0.34 V. Tl^+ should also be a poor reducing agent since the Tl^{3+}/Tl^+ potential is +1.25 V.

(14) The observation of four diastereoisomers requires that inversion of the sulfonium ion be slow on the NMR time scale. Slow inversion is expected assuming that the inversion barrier for **13** is within the reported range of 25–29 kcal/mol. Lambert, J. B. *Top. Stereochem.* **1971**, *6*, 19.

(15) ^1H NMR (300 MHz, acetone-d_6, δ vs. Me_4Si) with proton–proton couplings (Hz) defined according to the numbering scheme shown for 13. Major isomer: H_1, 1.22 (d, J_{12} = 9); H_2, 2.65 (dd, J_{21} = 9, J_{24} = 3.4); H_7, 2.78 (dd, J_{75} = 12.4, J_{76} = 0.5); H_3, 3.11 (t, J_{35} = J_{34} = 10.5); H_6, 3.64 (dd, J_{65} = 8.0, J_{67} = 0.5); H_4, 4.67 (ddd, J_{43} = 10.5, J_{45} = 5.5, J_{42} = 3.4); C_5H_5, 5.18 (s); H_5, 5.41 (m, J_{57} = 12.4, J_{53} = 10.5, J_{56} = 8.0, J_{54} = 5.5); *m*,*p*-C_6H_5, 7.59–7.74 (m); *o*-C_6H_5, 7.84–7.89 (m). Minor isomer: H_2, 2.36 (dd, J_{21} = 7.7, J_{25} = 2.7); H_7 2.76 (ddd, J_{75} = 12.8, J_{76} = 1.9, J_{74} = 1); H_6, 3.78 (dt, J_{65} = 8.7, J_{67} = 1.9, J_{64} = 1); H_3, 4.13 (dd, J_{34} = 12.1, J_{35} = 6.8); H_4, 4.28 (m, J_{43} = 12.1, J_{47} = I, J_{46} = 1); H_1, 4.42 (d, J_{12} = 7.7); H_5, 5.10 (m, J_{57} = 12.8, J_{56} = 8.7, J_{53} = 6.8, J_{52} = 2.7); C_5H_5, 5.15 (s); *m*,*p*-C_6H_5, 7.59–7.74 (m); *o*-C_6H_5, 7.84–7.89 (m).

(16) Four related compounds are known to us. Green reported $[\overline{FeCp(CO)CH_2OCH_2CH}=CH_2]$[1f] and $[\overline{FeCp(CO)C(O)ZCH(R)CH}=CH_2]$ (Z = O, NH, R = H; Z = CH_2, R = C_6H_7O) were prepared as mixtures of stereoisomers by Rosenblum and co-workers. Lennon, P.; Priester, W.; Rosan, A.; Madhavarao, M.; Rosenblum, M. *J. Organomet. Chem.* **1977**, *139*, C29.

(17) Identified on the basis of its ^1H NMR and mass spectrum: Cazes, B.; Guittet, E.; Julia, S.; Ruel, O. *J. Organomet. Chem.* **1977**, *177*, 67.

(18) Identified on the basis of its ^1H NMR spectrum: Kwart, H.; Evans, E. R. *J. Org. Chem.* **1966**, *31*, 413.

97375-01-4; **9**, 97375-03-6; **11**, 97375-05-8; **12**, 97375-07-0; **13**, 97375-08-1; A, 12107-38-9; B, 12244-83-6; [$FeCp(CO)_2CH_2OEt$], 12244-98-3; [$FeCp(CO)_2CH_2OC(O)CH_3$], 12244-91-6; [$FeCp(CO)(PMe_2Ph)_2$]$^+$, 83287-98-3; $TlBF_4$, 28625-02-7; PMe_2Ph, 672-66-2; NEt_3, 121-44-8; NC_5H_5, 110-86-1; $P(OMe)_3$, 121-45-9; $S(CH_3)_2$, 75-18-3; $S(CH_3)Ph$, 100-68-5; SPh_2, 139-66-2; $S(C_3H_5)Ph$, 5296-64-0; TlOEt, 20398-06-5; TlOAc, 563-68-8; bicyclo[6.1.0]-nonane, 286-60-2; cyclooctene, 931-88-4.

Electron-Promoted C–C Bond Formation. Novel Route to Tetrathiooxalate Derivatives

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Summary: The addition of $NaBH_4$ in THF to [$Fe(\eta^2\text{-}CS_2Me)(CO)_2L_2$]$^+PF_6^-$ (**1b**, L = PPh_3) gave the purple complex $Fe_2(\mu\text{-}\eta^2\text{-}S_2C_2(SMe)_2)(CO)_4(PPh_3)_2$ (**3**, 68%), whereas **1a** (L = PMe_3) under the same conditions afforded $Fe(\eta^2\text{-}HCS_2Me)(CO)_2(PMe_3)_2$ (**2a**). Complex **3** was transformed by exposure to air into a blue derivative, $Fe(\eta^2\text{-}S_2C_2(SMe)_2)(CO)_2PPh_3$ (**4**, 30–48%), the latter reaction being accelerated by the presence of acids, $Na^+PF_6^-$, or H_2O_2. By treatment with sodium amalgam complex **1b** also gave **3** which was transformed in situ into **4**. These reactions are consistent with electron transfer from hydride (or Na/Hg) to **1b**, C–C bond formation of the resulting radical giving **3** and oxidative cleavage of the Fe–Fe bond of **3** to produce **4**. X-ray structure characterizations of **3** and **4** are reported.

Heteroallenes constitute an important class of stable molecules whose activation by metal centers has been investigated extensively.[1,2] This activation is relevant to the synthesis of sulfur-containing organic compounds[3] and the modeling of reduction processes of CO_2,[1,4] especially with respect to C–C bond formation and/or its incorporation into organic substrates.[5] Examples of metal-promoted dimerization of heteroallenes have been reported to date, most of which involve the formation of carbon–heteroatom bonds in the so-called "head-to-tail" mode of coupling.[6]

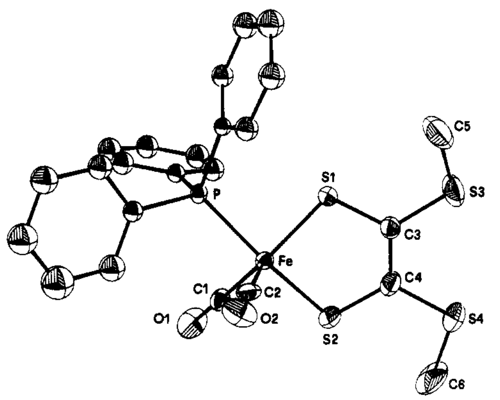
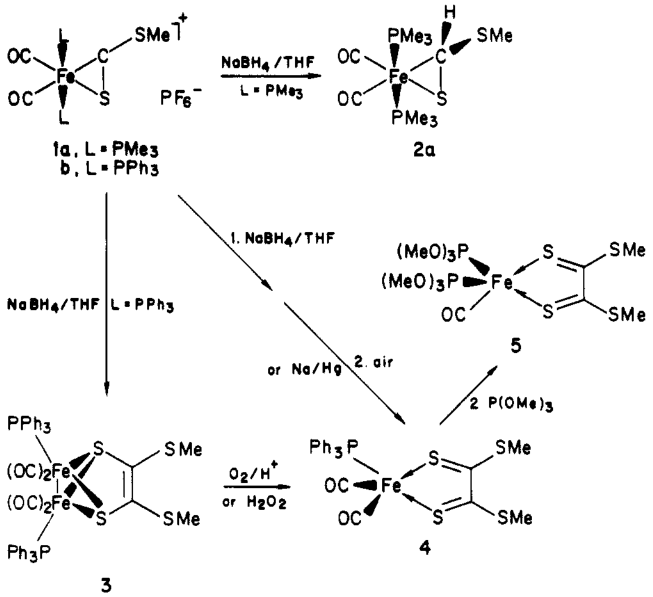


Figure 1. ORTEP view of $Fe(S_2C_2(SMe)_2)(CO)_2(PPh_3)$ (4). Selected bond lengths (Å) and angles (deg): Fe–S(1) = 2.163 (3), Fe–S(2) = 2.196 (3), Fe–P = 2.244 (3), S(1)–C(3) = 1.701 (10), S(2)–C(4) = 1.708 (12), C(3)–C(4) = 1.390 (15); S(1)–Fe–S(2) = 87.8 (1), S(1)–C(3)–C(4) = 118.0 (8), S(2)–C(4)–C(3) = 119.2(8).

Scheme I



Only recently have C–C bond formation processes involving heteroallenes been discovered.[7] We now report an interesting example of C–C bond formation with CS_2 as heteroallene which proceeds via electron transfer and leads to the formation of tetrathiooxalate derivatives. The reaction pathway is based on the X-ray structure determination of two key products.

The reaction of borohydride with a [$LnM(\eta^2\text{-}CS_2R)$]$^+$ cation has been shown to proceed in several ways: $Os(\eta^2\text{-}CS_2Me)(CO)_2(PPh_3)_2^+$ reacts with $NaBH_4$ to give $Os(H)(\eta^1\text{-}CS_2Me)(CO)_2(PPh_3)_2$[8] while [$N(CH_2CH_2PPh_2)_3Co(\eta^2\text{-}CS_2Me)$]$^+$ under similar conditions leads to SMe group elimination to form the thiocarbonyl ligand in [$N(CH_2CH_2PPh_2)_3Co(CS)$]BPh_4.[9] Recently we observed that

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