REDUCTIONS OF METAL CARBONYLS BY QUATERNARY AMMONIUM BOROHYDRIDES

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(Received March 24th, 1981)

Summary

Quaternary ammonium borohydrides, used directly or generated in phase transfer reactions, are highly effective reagents for preparing metal carbonyl anions from metal carbonyls [$Mo(CO)_6$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$ and $(\eta^5-C_5H_5)_2Mo_2(CO)_6$] and from some metal carbonyl halides [$BrMn(CO)_5$ and $\eta^5-C_5H_5Mo(CO)_3Cl$]. Where strongly basic anions would be formed from a halide [$BrMn(CO)_4PPh_3$ and $\eta^5-C_5H_5Ru(CO)_2Br$], the reactions provide efficient syntheses of the corresponding hydrides instead. The anion $\eta^5-C_5H_5Fe(CO)_2^-$ is not accessible by these techniques; reaction of $\eta^5-C_5H_5Fe(CO)_2Br$ yields the iron dimer (via the highly nucleophilic anion) and the dimer is unreactive toward $Q^+BH_4^-$. Reductions of $Re_2(CO)_{10}$ conducted in CH_2Cl_2 provide $Re_2(CO)_9Cl^-$ in high yield.

Introduction

Transition metal anions play a central role in the formation of compounds containing carbon—metal bonds [1] as well as in the synthesis of catalytically important metal cluster compounds [2]. The traditional way of generating metal carbonyl anions has been to treat a metal carbonyl dimer or halide with sodium amalgam [3]. Anions formed in this way are highly air-sensitive and often contaminated with mercury-containing compounds. More recently developed general methods are: a) reactions employing sodium-potassium alloy [4], b) cleavage reactions utilizing trialkylborohydrides [5] and c) reductions of metal carbonyl dimers by potassium hydride [6]. All of the newer methods are effective; but the reagents require special handling techniques and generate highly reactive alkali metal salts as products.

Noting that quaternary ammonium (Q) or bis(triphenylphosphine)iminium (PPN) cations have been effective in stabilizing reactive anions [7], we have sought to develop synthetic methods which would yield the Q salts directly.

We report herein the results of our efforts to use quaternary ammonium borohydrides, generated in two-phase reactions [8] or applied directly, to effect the reductions of metal carbonyls and metal carbonyl halides. These methods constitute convenient and effective means for performing conversions of most of these complexes to anions; in cases where highly basic anions would be formed, the metal carbonyl hydride is formed instead since $Q^+BH_4^-$ is not strongly basic. Adducts of the anions with BH_3, of the type reported by Parshall [9], if formed are not stable under our reaction conditions and are not observed. Also, the reaction conditions are sufficiently mild that BH_4 complexes [10] are not generated either. Since the starting reagents are not highly air-sensitive, neither vacuum lines nor Schlenk techniques are needed except in instances where isolation of an air-sensitive product is desired.

As in other reactions where borohydrides are used as reducing agents for metal carbonyls [11], formyl anions are presumed to be intermediates. The more vigorous reaction conditions needed for $Q^+BH_4^-$ reductions do not allow such intermediates to be observed, however.

Results and discussion

The reductions of metal carbonyls and metal carbonyl halides which have been done with quaternary ammonium borohydrides under phase transfer (PTC) conditions and by direct addition in homogeneous reactions are summarized in Table 1. Earlier [8], we compared the PTC-based syntheses of the anions from $BrMn(CO)_5$, η^5-$C_5H_5Mo(CO)_3Cl$, $Fe_3(CO)_{12}$ and $Co_2(CO)_8$ with existing methods for their preparation and those comparisons are not repeated

TABLE 1

REDUCTIONS OF METAL CARBONYLS BY $Q^+BH_4^-$ [a]

Starting material	Product isolated	PTC reaction [b]		homogeneous reaction [c]	
		time	yield(%)	time	yield(%)
$Fe_3(CO)_{12}$	$Et_4N^+HFe_3(CO)_{11}^-$	$\frac{1}{2}$ h	80	5 min	82
$Ru_3(CO)_{12}$	$Et_4N^+HRu_3(CO)_{11}^-$	24 h	very low	1 h	83
$Co_2(CO)_8$	$Ph_3SnCo(CO)_4$	$\frac{1}{2}$ h	83	5 min	80
$Re_2(CO)_{10}$	$Et_4N^+HRe_2(CO)_9Cl^-$	24 h	0	2 h	89
$Re_2(CO)_{10}$ [d]	$Et_4N^+HRe_2(CO)_9$	—	—	1 h	not determined
$Mn_2(CO)_{10}$ [e]	$Ph_3SnMn(CO)_5$	not determined		2 min	79
$Mo(CO)_6$	$Et_4N^+NMo_2(CO)_{10}^-$	$2\frac{1}{2}$–$3\frac{1}{2}$	64—70	$1\frac{1}{2}$ h	62
$Mo(CO)_6$ [d]	$Et_4N^+HMo_2(CO)_{10}^-$	—	—	1 h	65
$BrMn(CO)_4PPh_3$	$HMn(CO)_4PPh_3$	3 h	88	$1\frac{1}{2}$ h	81
$BrMn(CO)_5$	$Ph_3SnMn(CO)_5$	7 h [f]	95	30 min	68
η^5-$C_5H_5Mo(CO)_3Cl$	η^5-$C_5H_5Mo(CO)_3SnPh_3$	2 h [f]	81	30 min	71
η^5-$C_5H_5Ru(CO)_2Br$	η^5-$C_5H_5Ru(CO)_2H$	17 h	74	2 h	83
η^5-$C_5H_5Fe(CO_2Br$	$[\eta^5$-$C_5H_5Fe(CO)_2]_2$	—	—	not determined	
$[\eta^5$-$C_5H_5Fe(CO)_2]_2$	no reaction	—	—	7—15 h	—
$[\eta^5$-$C_5H_5Mo(CO)_3]_2$ [e]	η^5-$C_5H_5Mo(CO)_3SnPh_3$	—	—	2 h	83

[a] Reactions done in CH_2Cl_2 except as noted. [b] Reactions done with TEAB except as noted. [c] Reactions done with TEABH. [d] Reaction done in CH_3CN. [e] Reaction done in THF. [f] The phase transfer reagent was BTEAC.

here. In general, the PTC reactions are somewhat slower than reactions utilizing LiEt$_3$BH, KH or Na(K), but the product yields compare favorably.

Some additional metal carbonyl complexes have now been examined which were not studied by us earlier. The μ-hydride, HMo$_2$(CO)$_{10}^-$, is readily formed by either PTC or direct addition of tetraethylammonium borohydride (TEABH); these methods provide the μ-hydride in similar yields but much shorter times than existing methods [12]. Facile cleavage of Mn$_2$(CO)$_{10}$ by TEABH provides Mn(CO)$_5^-$ in slightly lower yield than the preparation of Gladysz [5]; the phase transfer method is not effective in cleaving Mn$_2$(CO)$_{10}$.

The product obtained from TEABH reduction of Re$_2$(CO)$_{10}$ in CH$_3$CN appears to be Et$_4$N$^+$HRe$_2$(CO)$_9^-$ (its spectral properties agree with those reported by Casey and Neumann [13]); however, a crystalline product could not be obtained. When the reduction is conducted in CH$_2$Cl$_2$, Et$_4$N$^+$Re$_2$(CO)$_9$Cl$^-$ is isolated instead of the hydrido anion. The halo anion can be formed independently by treatment of HRe$_2$(CO)$_9^-$ with CH$_2$Cl$_2$ (see Experimental). Although the exchange of hydrogen for halogen has been observed with other hydride complexes [14], this behavior seems to be more typical of neutral systems which have phosphorous ligands than of metal carbonyl anions. However, Bergman [15] has noted that η^5-C$_5$H$_5$V(CO)$_3$H$^-$ is readily converted to the corresponding halo anion by reactions with a variety of organic halides. The fact that both the η^5-C$_5$H$_5$V(CO)$_3$H$^-$ and HRe$_2$(CO)$_9^-$ are "ligand saturated" hydridic anions may be significant in determining their unusual behavior toward halogenated organic compounds.

In our earlier report of the generation of Et$_4$N$^+$HFe$_3$(CO)$_{11}^-$ from Fe$_3$(CO)$_{12}$ under phase transfer conditions [8], we noted that the method provided the trinuclear anion more readily and in higher yield than methods utilizing Fe(CO)$_5$. Recently, Shriver and his coworkers [16] have described the preparation of PPN$^+$HFe$_3$(CO)$_{11}^-$ from Fe(CO)$_5$ and Fe$_3$(CO)$_{12}$; the reaction with Fe$_3$(CO)$_{12}$ utilizes aqueous KOH and provides the anion in overall 77% yield after about an hour. Both the PTC reaction and the direct use of TEABH with Fe$_3$(CO)$_{12}$ provide the anion in higher yields after shorter times and, furthermore, the quaternary ammonium salt is obtained directly.

Although the trinuclear ruthenium cluster anion has been less well studied than its iron analog, there have been two recent preparations of Et$_4$N$^+$HRu$_3$(CO)$_{11}^-$ which have greatly improved its availability. The procedure of Lewis, et al., [17] utilizes Ru$_3$(CO)$_{12}$ with NaBH$_4$ followed by cation exchange and provides the Et$_4$N salt in overall 76% yield after about 1 day. The procedure of Ford and his coworkers [18] involves Ru$_3$(CO)$_{12}$ and aqueous KOH followed by cation exchange and provides the same salt in 70% overall yield after several hours. Our method provides the same product in higher yield after a much shorter reaction time from the same metal carbonyl when TEABH is used directly. The phase transfer method in CH$_2$Cl$_2$, however, yields a complex product mixture which has HRu$_3$(CO)$_{11}^-$ as one component. To this time, no attempt has been made to find optimum conditions for the generation of this anion by PTC.

In general, the conversions utilizing TEABH in homogeneous reactions proceed to completion more rapidly and give higher product yields than the corresponding phase transfer reactions. Only in the cases where BrMn(CO)$_5$ and

η^5-$C_5H_5Mo(CO)_3Cl$ are used to generate the anions or $BrMn(CO)_4PPh_3$ is converted to the hydride are the yields in the PTC reactions substantially better than those involving direct reaction of TEABH. The PTC method is clearly a milder technique but in some cases it is not effective. Direct use of TEABH is effective with most of the metal carbonyl complexes examined; it failed with η^5-$C_5H_5Fe(CO)_2Br$ because of the high nucleophilicity [19] of the iron anion and the lack of reactivity of the iron dimer. The η^5-$C_5H_5Fe(CO)_2^-$ is therefore not accessible by this technique whereas the less nucleophilic [19] η^5-C_5H_5Mo-$(CO)_3^-$ can be readily obtained from the halide or the molybdenum dimer.

Except for the reduction of $Cr(CO)_6$ to the μ-hydride (reported a number of years ago without experimental details [20]), we have found no other instances where $Q^+BH_4^-$ has been used to effect reductions of metal carbonyl complexes. Recent attempts to use $PPN^+BH_4^-$ to effect reductions have met with mixed success [10,21]. Quaternary ammonium ions appear to be effective in stabilizing metal carbonyl anions and are presently more economical to use than their PPN analog.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Benzene, hexane, acetonitrile, pentane and tetrahydrofuran were dried and distilled before use. The following compounds were prepared as described previously: $BrMn(CO)_5$ [22], cis-$BrMn(CO)_4PPh_3$ [23], η^5-$C_5H_5Ru(CO)_2Br$ [24], η^5-C_5H_5Fe-$(CO)_2Br$ [25], benzyltriethylammonium chloride (BTEAC) [26]. The Ph_3SnCl and tetraethylammonium hydroxide were obtained from Alfa Products; the tin compound was recrystallized from benzene before use. The $Fe_3(CO)_{12}$ (recrystallized from CH_2Cl_2/hexane), $[\eta^5$-$C_5H_5Mo(CO)_3]_2$, $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, Re_2-$(CO)_{10}$ and $Mo(CO)_6$ (all used directly) were obtained from Strem Chemicals. The $Co_2(CO)_8$ (recrystallized from pentane), $Mn_2(CO)_{10}$ (sublimed before use) and $Ru_3(CO)_{12}$ (used directly) were purchased from Pressure Chemical Co. Sodium borohydride, obtained from MCB, and tetraethylammonium bromide (TEAB), obtained from Aldrich, were used directly.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer and were calibrated against polystyrene film. ^1H NMR spectra were obtained on a Varian EM-390 or a Bruker WH-90DS spectrometer; peak positions are given in ppm downfield from TMS. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories.

Preparation of $Et_4N^+BH_4^-$ (TEABH) [27]

A solution of Et_4NOH in methanol (50 ml of 25% Et_4NOH, 106 mmol) was added to a stirred mixture of $NaBH_4$ (7.99 g, 211 mmol) in 57 ml of 10% methanolic NaOH. An additional 50 ml of CH_3OH was added to dissolve the remaining solid. The solution was stirred for 3 h and then solvent was removed on a rotary evaporator. The residue was extracted with three 100 ml portions of CH_2Cl_2 and the combined extracts were concentrated to 50 ml; $Et_4N^+BH_4^-$ was precipitated by addition of 150 ml of ether followed by cooling to $-20°C$.

The white powder was filtered, washed with ether, and dried under vacuum to yield 14.10 g (92%) of $Et_4N^+BH_4^-$.

Preparation of $Et_4N^+HFe_3(CO)_{11}^-$

a) Single phase method. A solution of $Fe_3(CO)_{12}$ (0.50 g, 1.00 mmol) and TEABH (0.14 g, 1.00 mmol) in 50 ml of CH_2Cl_2 was stirred at room temperature for 5 min, at which time the initial dark green color completely turned dark purple. The solution was washed with three 60 ml portions of water, dried over $MgSO_4$ and filtered. The solvent was removed by rotary evaporator and 0.56 g dark red powder was obtained. The crude $Et_4N^+HFe_3(CO)_{11}^-$ was purified by recrystallization from CH_2Cl_2/hexane; 0.498 g (82%) dark red-purple powder was obtained: IR ν(CO) (CH_2Cl_2) 2065w, 2000vs, 1970s, 1945(sh), 1720w cm^{-1} [Lit. [28] ν(CO) (CH_2Cl_2) 2070w, 2000vs, 1970s, 1946m, 1718m cm^{-1}].

b) Phase transfer method: A mixture of $Fe_3(CO)_{12}$ (0.50 g, 1.00 mmol) in 80 ml of CH_2Cl_2 and TEAB (0.31 g, 1.50 mmol), $NaBH_4$ (0.38 g, 10.0 mmol) in 50 ml of water was stirred at room temperature for 1/2 h. The dark red organic layer was separated and extracted with three 60 ml portions of water. The reddish water washings were extracted with 30 ml of CH_2Cl_2. The combined CH_2Cl_2 extracts were dried over $MgSO_4$. The solvent was removed by rotary evaporator and 0.545 g dark red solid was obtained. The red solid was recrystallized from CH_2Cl_2/hexane and 0.485 g (80%) dark red powder resulted. The spectral properties of the product were identical to those in a above.

Preparation of $Et_4N^+HRu_3(CO)_{11}^-$

a) Single phase method. A mixture of $Ru_3(CO)_{12}$ (0.48 g, 0.75 mmol) and TEABH (0.43 g, 3.00 mmol) in 75 ml of CH_2Cl_2 was stirred at room temperature for 1 h at which time the initial orange solution turned dark red. The reaction mixture was washed with 3 × 80 ml of water, dried over $MgSO_4$ and filtered. Solvent was removed under vacuum and 0.52 g dark red powder was obtained. The crude $Et_4N^+HRu_3(CO)_{11}^-$ was recrystallized from CH_2Cl_2/hexane and 0.46 g (83%) dark purple powder resulted; IR ν(CO) (CH_2Cl_2) 2075vw, 2020vs, 1985s, 1950(br, sh), 1700w cm^{-1}, [Lit. [17] 2073vw, 2014vs, 1984s, 1950m, 1691w cm^{-1}].

b) Phase transfer method. A mixture of $Ru_3(CO)_{12}$ (0.67 g, 1.04 mmol) in 100 ml of CH_2Cl_2 and $NaBH_4$ (0.39 g, 10.4 mmol), TEAB (0.356 g, 1.56 mmol) in 60 ml of water was heated at 45°C with stirring for 24 h; the mixture turned brown during this time. After the usual work-up, 0.734 g red-brown solid was obtained; IR ν(CO) (CH_2Cl_2) 2060m, 2018vs, 1998vs, 1970m, 1720w cm^{-1}. The product obtained was a mixture of $HRu_3(CO)_{11}^-$ and at least one other compound which seemed to be the anion previously identified as $Ru_6(CO)_{18}^{2-}$ [29]: IR ν(CO) (CH_2Cl_2) 2006s, 1986s, 1930w, 1754w cm^{-1}. No separation was attempted.

Preparation of $Ph_3SnCo(CO)_4$

a) Single phase method. A mixture of $Co_2(CO)_8$ (0.90 g, 2.64 mmol) and TEABH (0.76 g, 5.28 mmol) in 75 ml of CH_2Cl_2 was stirred at room temperature for 5 min. The light brown solution was washed with three 100 ml portions of water, dried over $MgSO_4$ and filtered; the filtrate showed a very strong

broad IR band at 1890 cm^{-1} [30]. To this solution, Ph$_3$SnCl (3.053 g, 7.92 mmol, 50% excess) was added and the mixture was stirred overnight and the solution turned green. The solvent was removed on a rotary evaporator and a greenish solid was obtained. Extraction of the residue with hot hexane, followed by crystallization afforded 2.20 g (80%) of pale yellow Ph$_3$SnCo(CO)$_4$: m.p. 121—122°C [Lit. [5] 119—121°C], IR (hexane) 2085s, 2025s, 1995vs cm^{-1} [Lit. [5] ν(CO) (THF) 2090m, 2025m, 1995s cm^{-1}].

b) *Phase transfer method.* A solution of BzEt$_3$N$^+$Co(CO)$_4^-$ was prepared from Co$_2$(CO)$_8$ (0.66 g, 1.93 mmol), NaBH$_4$ (0.73 g, 19.3 mmol), BTEAC (1.31 g, 5.79 mmol) in 80 ml of CH$_2$Cl$_2$ and 60 ml of water exactly in the same manner as described previously for Et$_4$N$^+$Co(CO)$_4^-$ [8]. After work up, a brown solution (IR ν(CO) 1890 cm^{-1}) was obtained; to this solution Ph$_3$SnCl (2.23 g, 5.79 mmol) was added and the mixture was stirred overnight. The crude product (2.02 g) was recrystallized as described above and 1.66 g (83%) of pure product were obtained.

Preparation of Et$_4$N$^+$Re$_2$(CO)$_9$Cl$^-$ [31]

a) *Single phase method.* A mixture of Re$_2$(CO)$_{10}$ (0.65 g, 1.00 mmol), TEABH (0.58 g, 4.00 mmol) dissolved in 130 ml of CH$_2$Cl$_2$ was stirred at room temperature for 2 h. The initially colorless solution gradually turned orange. The solution was extracted with 3 × 80 ml of water and then dried over MgSO$_4$ and filtered. The solvent was removed on a rotary evaporator and 0.737 g of yellow-orange solid was obtained. The crude product, Et$_4$N$^+$Re$_2$-(CO)$_9$Cl$^-$ was recrystallized from CH$_2$Cl$_2$/hexane and 0.70 g (89%) of yellow leaflets were obtained: m.p. 179—180°C (dec); IR ν(CO) (CH$_2$Cl$_2$) 2090vw, 2030m, 1980vs(br), 1930m, 1890m cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) 1.30 (tt, J(H—H) = 7.2 Hz, J(N—H$_\beta$) = 1.8 Hz, 12 H, NCH$_2$CH$_3$), 3.24 ppm (q, J = 7.5 Hz, 8 H, NCH$_2$CH$_3$). Found: C, 25.86; H, 2.60; N, 1.85; Cl, 4.68. calcd. for C$_{17}$H$_{20}$O$_9$-NClRe$_2$: C, 25.84; H, 2.55; N, 1.77; Cl, 4.49%.

b) *Phase transfer method.* A mixture of Re$_2$(CO)$_{10}$ (0.32 g, 0.50 mmol) in 50 ml of CH$_2$Cl$_2$ and NaBH$_4$ (0.18 g, 5.00 mmol), TEAB (0.15 g, 0.75 mmol) in 40 ml of water was stirred at room temperature for 19 h and no spectral change was noticed, but the organic layer turned pale yellow. Fresh NaBH$_4$ (0.18 g, 5.00 mmol) was added to the mixture at this point and the mixture was heated at 45°C for 6 h. IR spectral examination showed no evidence of reaction.

Preparation of Et$_4$N$^+$HRe$_2$(CO)$_9^-$ and conversion to Et$_4$N$^+$Re$_2$(CO)$_9$Cl$^-$

A mixture of Re$_2$(CO)$_{10}$ (0.65 g, 1.00 mmol) and TEABH (0.58 g, 4.00 mmol) in 50 ml of CH$_3$CN was heated at 80°C for 1 h and the initial pale yellow solution turned dark orange in color. The mixture was cooled and then transferred to a Schlenk vessel under N$_2$. The solvent was removed using a vacuum line and an orange-yellow semi-solid material was obtained: IR ν(CO) (CH$_3$CN) 2085vw, 2020mw, 1970s, 1925m, 1890m cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.38 (tt, NCH$_2$CH$_3$), 3.48 (q, NCH$_2$CH$_3$), —7.05 ppm (s, Re—H) [The hydrido compound Et$_4$N$^+$HRe$_2$(CO)$_9^-$, prepared previously [13], has the following spectral properties: IR ν(CO) (THF) 2078vw, 2028m, 1972s, 1924wm, 1888m cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.40 (tt), 3.50 (q), —7.10 ppm (s)].

Every attempt to crystallize the hydride from several preparations failed. The crude material from this reaction was dissolved in 60 ml of CH_2Cl_2 and stirred at room temperature for $1\frac{1}{2}$ h then washed with 3 × 50 ml of water and dried over $MgSO_4$. The solvent was removed with a rotary evaporator and 0.67 g semi-solid was obtained. The product was recrystallized from CH_2Cl_2/hexane and 0.55 g (69%) yellow-orange plates were obtained; the spectral properties of the product ($Et_4N^+Re_2(CO)_9Cl^-$) were identical with those described for the chloride above.

Preparation of $Et_4N^+HMo_2(CO)_{10}^-$

a) Single phase method. (1) in CH_2Cl_2 solution: $Mo(CO)_6$ (1.00 g, 3.79 mmol) and TEABH (0.55 g, 3.79 mmol) were dissolved in 80 ml of CH_2Cl_2 and refluxed under nitrogen with magnetic stirring. After $1\frac{1}{2}$ h the $Mo(CO)_6$ was essentially consumed and carbonyl bands at 2043w, 1940vs, and 1875s cm^{-1} together with carbonyl bands of weaker intensity at 2020, 1910 and 1830 cm^{-1} appeared. The μ-hydride, $Et_4N^+HMo_2(CO)_{10}^-$, accounted for the carbonyl bands at 2043, 1940, and 1875 cm^{-1}; other bands at 2020, 1910 and 1830 cm^{-1} resulted from side product(s) not identified. The solution was then extracted with 30 ml of water and then dried over $MgSO_4$. The IR $\nu(CO)$ (CH_2Cl_2) of the solution after drying and filtration indicated predominantly the presence of $Et_4N^+HMo_2(CO)_{10}^-$ and a slight amount of $Mo(CO)_6$. Removal of the CH_2Cl_2 and recrystallization of the residue from THF-hexane resulted in 0.711 g (62%) of the yellow $Et_4N^+HMo_2(CO)_{10}^-$. The product had an IR $\nu(CO)$ (THF): 2041w, 1942vs, 1878s cm^{-1} [Lit. [12] $\nu(CO)$ (THF): 2035w, 1920vs, 1860s cm^{-1}] and ^1H NMR (μ-hydrido proton; THF): −12.2 ppm [Lit. [12] −12.15 ppm (THF)].

2) In CH_3CN solution: $Mo(CO)_6$ (0.50 g, 1.89 mmol), was dissolved in 30 ml of CH_3CN by heating the solution under a nitrogen atmosphere in an oil bath maintained at 50°C. TEABH (0.27 g, 1.89 mmol) in 10 ml of CH_3CN was rapidly added to the solution and the temperature raised to 60°C (oil bath temperature). After 1 h, conversion of the $Mo(CO)_6$ was complete with no apparent formation of soluble by-products. However, a white solid (0.05 g) separated from the solution; this material was not identified. The mixture was filtered and the filtrate evaporated to dryness. Recrystallization of the brownish residue from THF-hexane resulted in 0.37 g (65% yield) of the $Et_4N^+HMo_2(CO)_{10}^-$.

b) Phase transfer method. In CH_2Cl_2 solution: $Mo(CO)_6$, 1.00 g (3.79 mmol), was dissolved in 45 ml of CH_2Cl_2. A mixture of sodium borohydride 0.71 g (18.9 mmol) and TEAB, 3.98 g (18.9 mmol), in 25 ml of water was rapidly added to the $Mo(CO)_6$ solution, and then refluxed gently at 57°C (oil bath temperature) under nitrogen with stirring. Conversion of the $Mo(CO)_6$ to the $Et_4N^+HMo_2(CO)_{10}^-$ was essentially complete after 3 h and 30 min, with no apparent formation of by-products. After removal of the aqueous layer the CH_2Cl_2 solution was washed, dried, and evaporated to dryness (as above); the residue was recrystallized from THF-hexane and produced 0.795 g (70% yield) of the yellow $Et_4N^+HMo_2(CO)_{10}^-$.

When a second reaction was done at 85°C (oil bath temperature), conversion of the $Mo(CO)_6$ to the $Et_4N^+HMo_2(CO)_{10}^-$ was essentially complete after 2 h

and 30 min. The final product after washing, drying and evaporating of the CH_2Cl_2 resulted in yellow-orange product; recrystallization from THF-hexane resulted in 0.73 g (64%) of the yellow $Et_4N^+HMo_2(CO)_{10}{}^-$.

Preparation of $Ph_3SnMn(CO)_5$ from $Mn_2(CO)_{10}$

a) Phase transfer method. Dimanganese decacarbonyl (0.50 g, 1.28 mmol), in 25 ml of CH_2Cl_2 was added dropwise during 35 min to a stirred solution of $NaBH_4$ (0.24 g, 6.41 mmol) and TEAB (1.34 g, 6.41 mmol) in 20 ml of water and 10 ml of CH_2Cl_2 under a nitrogen atmosphere with vigorous refluxing at 72°C (oil bath temperature).

After complete addition of the $Mn_2(CO)_{10}$ solution there was slight formation of the anion [$Et_4N^+Mn(CO)_5{}^-$] observed by IR after 2 h. However, when refluxing was continued for an additional $3\frac{1}{2}$ h the anion had partially decomposed with no additional conversion of the manganese dimer. The yield was not determined.

b) Single phase method. $Mn_2(CO)_{10}$ (0.50 g, 1.28 mmol) and TEABH (0.74 g, 5.13 mmol) were added together into 40 ml of refluxing THF under N_2 with magnetic stirring. After 2 min, conversion of the $Mn_2(CO)_{10}$ was complete as evidenced by an IR spectrum: vigorous gas evolution was noted as soon as the reagents were added together. After cooling to room temperature, 25 ml of saturated aqueous NaCl solution was added and the mixture was stirred for a few minutes. The aqueous layer was then removed and 0.99 g (2.57 mmol) of triphenyltin chloride was added and the resulting mixture was stirred for an hour. The solution was then dried over $MgSO_4$, filtered and evaporated to dryness on a rotary evaporator. The residue was extracted with hot hexane followed by hot hexane-CH_2Cl_2 and the combined extracts were evaporated to dryness. Recrystallization of the crude product from CH_2Cl_2-hexane afforded 1.10 g (79%) of pure product: m.p. 148—150.5°C (Lit. [5] 148—150°C) and IR ν(CO) (CH_2Cl_2) 2095m and 1995vs cm^{-1} [Lit. [5] (THF) 2090m and 1995vs cm^{-1}].

Preparation of cis-$HMn(CO)_4PPh_3$ from cis-$BrMn(CO)_4PPh_3$

a) Single phase method. A mixture of cis-$BrMn(CO)_4PPh_3$ (0.51 g, 1.00 mmol) and TEABH (0.58 g, 4.00 mmol) in 50 ml of CH_2Cl_2 was stirred at room temperature for $1\frac{1}{2}$ h. The solution was extracted with 3 × 30 ml of water, dried over $MgSO_4$ and filtered into a Schlenk vessel. The solvent was removed on a vacuum line and a yellow-brown solid was obtained. The crude product was extracted with 2 × 50 ml of degassed pentane; evaporation of the solvent on a vacuum line gave 0.35 g (81.4%) of yellow $HMn(CO)_4PPh_3$: IR ν(CO) (pentane) 2060m, 1985s, 1965vs, 1950s cm^{-1} [Lit. [32] IR ν(CO) (hexane) 2060, 1985, 1969, 1958 cm^{-1}] and ^1H NMR ($CDCl_2$): δ 7.40 (s, phenyl protons) and —7.28 ppm (d, Mn—H, J(P—H) = 33 Hz) [Lit. [33b] δ —6.94 ppm (d, J(P—H) = 34 Hz)].

b) Phase transfer method. A mixture of cis-$BrMn(CO)_4PPh_3$ (0.51 g, 1.00 mmol) in 30 ml of CH_2Cl_2 together with $NaBH_4$ (0.38 g, 10.0 mmol) and BTEAC (0.34 g, 1.50 mmol) in 30 ml of water was degassed and stirred at room temperature in a Schlenk vessel for 3 h. The organic layer was separated, extracted with 2 × 20 ml of water and dried over $MgSO_4$. The solvent was

removed on a vacuum line and a brown solid was obtained. Extraction with 2×50 ml of degassed hexane, followed by removal of the solvent gave 0.38 g (88%) of yellow product, m.p. 134—135°C [Lit. [33,32], 137.5°C, 132—133°C] with the same IR $\nu(CO)$ bands as described above.

Preparation of $Ph_3SnMn(CO)_5$ from $BrMn(CO)_5$

a) Single phase method. Manganese pentacarbonyl bromide (0.50 g, 1.82 mmol), was dissolved in 40 ml of CH_2Cl_2 and added dropwise during 25 min to a refluxing solution of TEABH (1.06 g, 7.30 mmol) in 50 ml of CH_2Cl_2 with magnetic stirring. After addition, the mixture was allowed to cool, and triphenyltin chloride (0.70 g, 1.82 mmol) was added directly to the reaction mixture; conversion of the anion to the triphenyltin derivative was complete within 15 minutes. The solution was extracted with 30 ml of water and then dried with $MgSO_4$ and filtered. An IR spectrum of the filtrate indicated the presence of the tin derivative and an unknown side product, $\nu(CO)$ 2040m, 2000m, 1955(sh), 1915s(br) cm^{-1}. After evaporation of the solvent, the residue was extracted with hot hexane followed by hot CH_2Cl_2-hexane. The extracts were combined and, after removal of the solvents, afforded pure $Ph_3SnMn(CO)_5$ (0.67 g, 68% yield) which was identical to the product described above.

b) Phase transfer method. A solution of $BrMn(CO)_5$ (0.27 g, 1.00 mmol) in 30 ml of CH_2Cl_2 was added slowly from a constant addition funnel to a stirring mixture of $NaBH_4$ (0.38 g, 10.0 mmol) and BTEAC (0.34 g, 1.50 mmol) in 30 ml of water and 30 ml of CH_2Cl_2 at room temperature during 7 h. At the end of the addition, the aqueous layer was siphoned out and the organic layer was washed with 2×25 ml of water. After separation of the water, anhydrous $MgSO_4$ was added and the mixture was stirred for a few minutes. An IR spectrum of this solution showed bands for $Mn(CO)_5^-$ at 1910s, 1860vs cm^{-1}. [Lit. [5] 1910s, 1860vs cm^{-1}]. The Ph_3SnCl (0.58 g, 1.50 mmol) was added and the mixture was stirred at room temperature for 1/2 hour then filtered and the solvent removed under vacuum; extraction of the residue with hot hexane followed by crystallization afforded 0.52 g (95%) white $Ph_3SnMn(CO)_5$.

Preparation of η^5-$C_5H_5Mo(CO)_3SnPh_3$ from η^5-$C_5H_5Mo(CO)_3Cl$

a) Single phase method. Cyclopentadienylmolybdenum tricarbonyl chloride [34] (0.50 g, 1.78 mmol) and TEABH (0.78 g, 5.35 mmol) were dissolved in 60 ml of CH_2Cl_2 at ambient temperature, under nitrogen with magnetic stirring; conversion to the anion was complete within 30 min and the mixture was then extracted with 30 ml of water. After removal of the water extract by pipet, triphenyltin chloride (0.69 g, 1.78 mmol), was added and the mixture was stirred for 45 min; IR spectral examination indicated that conversion to the tin derivative was complete.

The reaction mixture was then extracted with another 30 ml of water, dried with $MgSO_4$, filtered, and the filtrate evaporated to dryness. Crystallization from CH_2Cl_2/hexane gave 0.75 g (71%) η^5-$C_5H_5Mo(CO)_3SnPh_3$: m.p. 211—214°C [Lit. [5] 215—216°C)] and IR $\nu(CO)$ (CH_2Cl_2) 2000s, 1930m, 1900s cm^{-1} (Lit. [35] 2004, 1934, 1909 cm^{-1}.)

b) Phase transfer method. Cyclopentadienylmolybdenum tricarbonyl chloride

(1.00 g, 3.56 mmol) was dissolved in 40 ml of CH_2Cl_2 and added dropwise to a solution of BTEAC (1.22 g, 5.35 mmol) and $NaBH_4$ (0.67 g, 17.8 mmol) in 40 ml of water and 10 ml of CH_2Cl_2 at room temperature. After the addition was complete, ca. $1\frac{1}{4}$ h, the solution was stirred for an additional 45 min. After this time, conversion of the starting chloride to the anion was complete. The aqueous layer was separated, and the organic layer was extracted with 40 ml of water. Triphenyltin chloride (1.51 g, 3.92 mmol) dissolved in 15 ml of CH_2Cl_2 was added to the solution of the anion; conversion to the derivative was complete within 15—20 min. The solution was extracted with 20 ml of water and then dried over $MgSO_4$. Solvent was removed on a rotary evaporator and the crude product was recrystallized from CH_2Cl_2-hexane: yield 1.71 g (81%) of pale yellow η^5-$C_5H_5Mo(CO)_3SnPh_3$.

Preparation of η^5-$C_5H_5Ru(CO)_2H$ from η^5-$C_5H_5Ru(CO)_2Br$

   a) Single phase method. A mixture of η^5-$C_5H_5Ru(CO)_3Br$ (0.60 g, 2.00 mmol) and TEABH (1.16 g, 8.00 mmol) in 60 ml of CH_2Cl_2 was heated at 45°C for 2 h (some white solid was precipitated during this time.) The mixture was cooled and extracted with 3 × 60 ml of water, then dried over $MgSO_4$. The slurry was filtered through Celite into a Schlenk flask and CH_2Cl_2 was removed on a vacuum line at —5°C. A brownish oily residue was obtained which was extracted with 2 × 50 ml of degassed pentane. The pale yellow pentane extracts were filtered through Celite and $MgSO_4$. The solvent was then removed at —5°C on a vacuum line and the hydride, a pale yellow vile-smelling oil (0.37 g, 83%), was obtained: IR ν(CO) (pentane) 2035s, 1975s cm^{-1} [Lit. [36] ν(CO) (hexane) 2033s, 1973s cm^{-1}] and ^{1}H NMR (C_6D_{12}): δ 5.25 (s, C_5H_5) and —10.95 ppm (s, Ru—H) [Lit. [37] (C_6H_{12}): δ 5.16 and —10.92 ppm].

   b) Phase transfer method. A mixture of η^5-$C_5H_5Ru(CO)_2Br$ (0.60 g, 2.00 mmol) in 65 ml of CH_2Cl_2 and $NaBH_4$ (0.76 g, 20.0 mmol), TEAB (0.63 g, 3.00 mmol) in 55 ml of H_2O was heated at 45°C for 17 h. The organic layer was cooled and the product, η^5-$C_5H_5Ru(CO)_2H$, was isolated as an oil in the same manner as described above for the single phase method. The yield of the hydride was 0.33 g (74%).

Attempted preparation of η^5-$C_5H_5Fe(CO)_2^-$ from η^5-$C_5H_5Fe(CO)_2Br$

   Cyclopentadienyliron dicarbonyl bromide (0.15 g, 0.58 mmol) was dissolved in 10 ml of CH_2Cl_2 and added dropwise, with stirring, to a mixture of BTEAC (0.20 g, 0.88 mmol) and $NaBH_4$ (0.11 g, 2.9 mmol) in 10 ml of water and 5 ml of CH_2Cl_2. After about 45 min, approximately 1/3 of the iron halide had been added; an IR spectrum of the reaction mixture showed a small amount of conversion to $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, the only detectable product. Neither addition of more $NaBH_4$ nor heating to reflux caused conversion to the desired anion. Complete conversion of the bromide to the iron dimer appeared to take place but the yield was not determined.

Attempted preparation of η^5-$C_5H_5Fe(CO)_2^-$ from $[\eta^5$-$C_5H_5Fe(CO)_2]_2$

   Single phase method. Cyclopentadienyliron dicarbonyl dimer (0.50 g, 1.4 mmol) was added directly, in three portions at 15 min intervals to a solution of TEABH (0.41 g, 2.8 mmol) in 25 ml of CH_2Cl_2. No reaction was evident

(from IR spectra of the reaction mixture) after stirring for 7 h at room temperature, nor after an additional 15 h at reflux temperature.

In a second reaction, 0.50 g (1.4 mmol) of the iron dimer was mixed with 0.82 g (5.65 mmol) of TEABH in 40 ml of THF and the mixture refluxed for $3\frac{1}{2}$ h under N_2 with stirring. There was no evidence (by IR) of conversion to the anion during this time.

Preparation of η^5-$C_5H_5Mo(CO)_3SnPh_3$ from $[\eta^5$-$C_5H_5Mo(CO)_3]_2$

The dimer (0.50 g, 1.02 mmol) was dissolved in 30 ml of THF and a solution of TEABH (0.59 g, 4.08 mmol) in 20 ml of THF was added rapidly to it. The mixture was refluxed with stirring under an atmosphere of nitrogen for 1 h and 45 min; conversion to the anion was complete as evidenced by IR spectra. During the reaction, a tan precipitate formed; when reaction was complete, 25 ml of brine was added and the precipitate dissolved with gas evolution. With the addition of brine solution, the organic layer separated and the aqueous layer was removed. To the THF solution was added 0.79 g (2.04 mmol) of Ph_3SnCl in 10 ml of THF; conversion to η^5-$C_5H_5Mo(CO)_3SnPh_3$ was complete after 20 min of stirring at room temperature. The solution was dried over $MgSO_4$ then filtered and concentrated to dryness on a rotatory evaporator. The pale yellow residue was recrystallized from CH_2Cl_2-hexane to afford the pure product (1.00 g, 83%). The product was identical to that prepared from η^5-C_5H_5-$Mo(CO)_3Cl$ described above.

Acknowledgement

References

1 J.E. Ellis, J. Organometal. Chem., 86 (1975) 1.
2 See G.L. Geoffroy, Accts. Chem, Res., 13 (1980) 469 and ref. cited therein.
3 See R.B. King, Accts. Chem. Res., 3 (1970) 417 and ref. cited therein.
4 J.E. Ellis and E.A. Flom, J. Organometal. Chem., 99 (1975) 263.
5 J.A. Gladysz, G.M. Williams, W. Tam, D.L. Johnson, D.W. Parker and H.C. Selover, Inorg. Chem., 18 (1979) 553.
6 K. Inkrott, R. Goetze and S.G. Shore, J. Organometal. Chem., 154 (1978) 337.
7 a) J.K. Ruff and W.J. Schlientz, Inorg. Chem., 15 (1974) 84, b) R.D. Wilson and R. Bau, J. Amer. Chem. Soc., 96 (1974) 7601, and c) C.P. Casey and D. Scheck, ibid., 102 (1980) 2728.
8 A preliminary account of some of the two phase reductions has appeared: D.H. Gibson, F.U. Ahmed and K.R. Phillips, J. Organometal. Chem., 206 (1981) C17.
9 G.W. Parshall, J. Amer. Chem. Soc., 86 (1964) 361.
10 S.W. Kirtley, M.A. Andrews, R. Bau, G.W. Grynkewich, T.J. Marks, D.L. Tipton and B.R. Whittlesey, J. Amer. Chem. Soc., 99 (1977) 7155.
11 See ref. 5 and refs. cited therein.
12 R.G. Hayter, J. Amer. Chem. Soc., 88 (1966) 4376.
13 C.P. Casey and S.M. Neumann, J. Amer. Chem. Soc., 100 (1978) 2544.
14 a) B.L. Booth and R.M. Hazeldine, J. Chem. Soc. (A), (1966) 157, b) D.H. Gerlach, W.G. Peet and E.L. Muetterties, J. Amer. Chem. Soc., 94 (1972) 4545, and c) B.L. Booth and B.L. Shaw, J. Organometal. Chem., 43 (1972) 369.
15 R.J. Kinney, W.D. Jones and R.G. Bergman, J. Amer. Chem. Soc., 100 (1978) 7902.
16 H.A. Hodali, C. Arcus and D.F. Shriver, Inorg. Syn., 20 (1980) 218.

17 B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Suss, J. Chem. Soc., Dalton, (1979) 1356.
18 C. Ungermann, V. Landis, S.A. Moya, H. Cohen, H. Walker, R.G. Pearson, R.G. Rinker and P.C. Ford, J. Amer. Chem. Soc., 101 (1979) 5922.
19 See R.B. King, Accts. Chem. Res., 3 (1970) 417 and ref. cited therein.
20 L.B. Hardy, P.M. Treichel, L.F. Dahl and R.G. Hayter, J. Amer. Chem. Soc., 88 (1966) 366.
21 B.F.G. Johnson, R.L. Kelly, J. Lewis and J. Thornback, J. Organometal. Chem., 190 (1980) C91.
22 M.H. Quick and R.J. Angelici, Inorg. Syn., 19 (1979) 160.
23 A.M. Bond, R. Colton and M.E. McDonald, Inorg. Chem., 17 (1978) 2842.
24 D.H. Gibson, W.-L. Hsu, A.L. Steinmetz and B.V. Johnson, J. Organometal. Chem., 208 (1981) 89.
25 B.F. Hallam and P.L. Pauson, J. Chem. Soc., (1956) 3030.
26 Prepared according to the general procedure described by Herriott and Picker [J. Amer. Chem. Soc., 97 (1975) 2345].
27 a) M.D. Banus, R.W. Bragdon and T.R.P. Gibb, Jr., J. Amer. Chem. Soc., 74 (1952) 2346, and b) R.K. Hertz, H.D. Johnson, II, and S.G. Shore, Inorg. Syn., 17 (1977) 21.
28 J.R. Wilkinson and L.J. Todd, J. Organometal. Chem., 118 (1976) 199.
29 C.R. Eady, B.F.G. Johnson, J. Lewis, M.C. Malatesta, P. Machin and P. McPartin, J. Chem. Soc., Chem. Commun., (1976) 945.
30 The $Et_4N^+Co(CO)_4^-$ shows only one $\nu(CO)$ band; see ref. 8.
31 Comparison of the number and relative intensities of the IR spectral bands of this compound with those of $HRe_2(CO)_9^-$ ([13] suggests that they may have the same (cis) geometry.
32 J.A. Froelich and D.J. Darensbourg, Inorg. Chem., 16 (1977) 960.
33 a) W. Hieber, G. Faulhaber and F. Theubert, Z. Anorg. Allg. Chem., 315 (1962) 125, and b) W. Hieber and H. Duchatsch, Chem. Ber., 98 (1965) 2933.
34 This compound was prepared by modification of an existing procedure [C. White and R.J. Mawby, Inorg. Chim. Acta, 4 (1970) 261]: $[\eta^5-C_5H_5Mo(CO)_3]_2$ was photolyzed in $CHCl_3$ under N_2 with an unfiltered 450 W Ace-Hanovia UV lamp (immersion system). When 5 g of the molybdenum dimer was used (in 250 ml $CHCl_3$), the reaction was complete after an hour and afforded the chloride, cleanly, as the sole product.
35 H.R.H. Patil and W.A.G. Graham, Inorg. Chem., 5 (1966) 1401.
36 A.P. Humphries and S.A.R. Knox, J. Chem. Soc., Dalton, (1975) 1710.
37 A. Davison, J.A. McCleverty and G. Wilkinson, J. Chem. Soc., (1963) 1133.