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REACTION OF PENTACARBONYL-MANGANESE(—I) AND -RHENIUM(—I) WITH METAL CARBONYL HALIDE DERIVATIVES

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Summary

Studies are reported related to the reaction of $M(CO)_5^-$ (M = Mn, Re) with $XM(CO)_3L$, $XM(CO)_5$, and $XRe(CO)_3(pyridine)_2$ (X = Cl, Br, I; M = Mn, Re; L = 2,2'-bipyridine, 1,10-phenanthroline, 1,2-bis(diphenylphosphino)ethane, 2,2'-biquinoline, 4,7-diphenyl-1,10-phenanthroline, *o*-phenylenebis(dimethylarsine), and *cis*-1,2-bis(diphenylphosphino)ethylene) which may yield metal—metal bonded complexes. Neither $XM(CO)_5$ nor $XRe(CO)_3(pyridine)_2$ react at 25°C, and for $XM(CO)_3L$ only those complexes which are easily reduced (L = 2,2'-bipyridine, 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, and 2,2'-biquinoline) readily yield products of the formula $M_2(CO)_8L$. The data suggest that the metal—metal bond formation is not via a simple nucleophilic attack mechanism but likely involves prior electron transfer to generate $XM(CO)_3L^{\cdot-}$.

Synthesis of metal—metal bonded complexes by reaction of a metal carbonyl anion with a metal carbonyl halide is an accepted procedure [1], and we employed [2] such a route in preparing $Re_2(CO)_8$(1,10-phenanthroline) (reaction 1). Our interest was aroused in this reaction class when we were unable to prepare $Re_2(CO)_8(pyridine)_2$ by reaction of $Re(CO)_5^-$ with $ClRe(CO)_3(pyridine)_2$.

$$Re(CO)_5^- + ClRe(CO)_3(1,10\text{-phenanthroline}) \rightarrow Cl^- + (OC)_5Re{-}Re(CO)_3(1,10\text{-phenanthroline}) \quad (1)$$

It is well established that metal carbonyl anions can behave as straight-forward nucleophiles in substitution reactions of Group IV halides [3]. Additionally, metal carbonyl anions are capable of behaving as one-electron reducing agents in such circumstances [4]. In this paper we provide evidence that reaction 1 oc-

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curs via an electron transfer mechanism and not by simple associative nucleophilic displacement of the halide. Such a mechanism has precedence from the work of Dessy and Weissman [5].

Results and discussion

a. Reaction of $M(CO)_5^-$ with $XM(CO)_3L$. Our main results are for the reaction of $Re(CO)_5^-$ with $XRe(CO)_3L$. These will be amplified with some information for the Mn analogues below. For certain $XRe(CO)_3L$ complexes we find that reaction at 25°C with $Re(CO)_5^-$ efficiently and rapidly yields metal—metal bonded $Re_2(CO)_8L$. In other cases we have found no reaction even upon heating the mixture. In particular, the comparison of the behavior of *fac*-$ClRe(CO)_3$(pyridine)$_2$ (unreactive) with *fac*-$ClRe(CO)_3$(2,2'-bipyridine) (reactive) is striking. The *fac*-$ClRe(CO)_3$(pyridine)$_2$ can be quantitatively recovered after refluxing it in THF solutions of excess $Re(CO)_5^-$ for several hours, while even at 25°C one quantitatively generates $Re_2(CO)_8$(2,2'-bipyridine) when $ClRe(CO)_3$(2,2'-bipyridine) and $Re(CO)_5^-$ are mixed. A comparison of the relative rates of reactive $XRe(CO)_3L$ complexes and a list of non-reactive ones are given in Table 1. Representative spectral changes accompanying reaction of $Re(CO)_5^-$ with $XM(CO)_3L$ are shown in Fig. 1, and plots of initial optical density change as a function of reaction time are given in Fig. 2. We note additionally that $Re(CO)_5^-$ and $Mn(CO)_5^-$ react with $BrMn(CO)_3$(1,10-phenanthroline) to yield $(OC)_5ReMn(CO)_3$(1,10-phenanthroline) and $Mn_2(CO)_8$(1,10-phenanthroline), respectively. However, we fail to get reaction of $ClRe(CO)_3$(1,10-phenanthroline) and $Mn(CO)_5^-$.

b. Reduction of $XM(CO)_3L$. The difference in behavior of $ClRe(CO)_3$(pyridine)$_2$

TABLE 1

RELATIVE REACTIVITY OF METAL CARBONYL HALIDES WITH $Re(CO)_5^-$ [a]

Metal carbonyl halide	Initial relative rate [b]	Product [expected product]
$ClRe(CO)_3$(2,2'-bipyridine)	1.0	$Re_2(CO)_8$(2,2'-bipyridine)
$ClRe(CO)_3$(2,2'-biquinoline)	2.6	$Re_2(CO)_8$(2,2'-biquinoline)
$ClRe(CO)_3$(4,7-diphenyl-1,10-phenanthroline)	2.7	$Re_2(CO)_8$(4,7-diphenyl-1,10-phenanthroline)
$ClRe(CO)_3$(1,10-phenanthroline)	3.2	$Re_2(CO)_8$(1,10-phenanthroline)
$BrRe(CO)_3$(1,10-phenanthroline)	3.2	$Re_2(CO)_8$(1,10-phenanthroline)
$IRe(CO)_3$(1,10-phenanthroline)	2.4	$Re_2(CO)_8$(1,10-phenanthroline)
$BrMn(CO)_3$(1,10-phenanthroline)	Reacts [c]	$(OC)_5ReMn(CO)_3$(1,10-phenanthroline)
$ClRe(CO)_3$(pyridine)$_2$	[g]	[$Re_2(CO)_8$(pyridine)$_2$]
$ClRe(CO)_3$(diars) [d]	[g]	[$Re_2(CO)_8$(diars)]
$ClRe(CO)_3$(diphos) [e]	[g]	[$Re_2(CO)_8$(diphos)]
$ClRe(CO)_3$(2-phos) [f]	[g]	[$Re_2(CO)_8$(2-phos)]
$ClRe(CO)_5$	[g]	[$Re_2(CO)_{10}$]

[a] Reaction in dry, deoxygenated THF at 25°C. The metal carbonyl halide concentration was 4.3×10^{-4} *M* and $NaRe(CO)_5$ was 5×10^{-5} *M*. [b] Rates relative to $ClRe(CO)_3$(2,2'-bipyridine). Rate = 1.0 corresponds to initial rate of 3.7×10^{-6} *M* min^{-1}. This corresponds to a reaction half-time of ~1 h. [c] Relative rate not measured. [d] diars ≡ *o*-phenylenebis(dimethylarsine), [e] diphos ≡ 1,2-bis(diphenylphosphino)ethane. [f] 2-phos ≡ *cis*-1,2-bis(diphenylphosphino)ethylene. [g] No reaction.

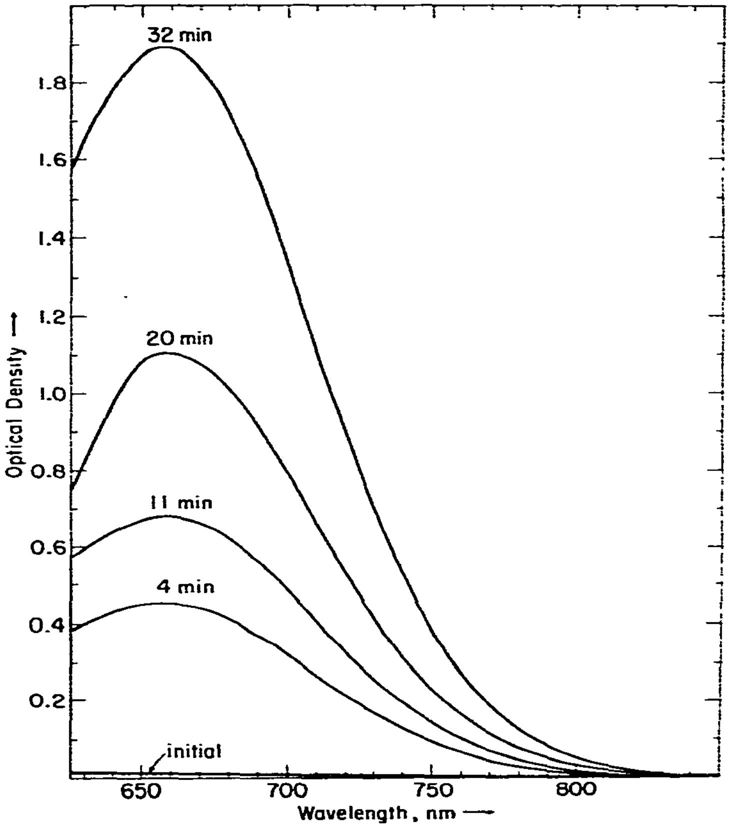

Fig. 1. Low energy visible electronic spectral changes accompanying reaction of 5 × 10^{-3} *M* $Re(CO)_5^-$ with 4.3 × 10^{-4} *M* $ClRe(CO)_3$(2,2'-biquinoline) in deoxygenated, dry THF at 298 K. The cell path length is 1.0 cm. The product is $Re_2(CO)_8$(2,2'-biquinoline); λ_{max} 660 nm (ϵ 6200 mol^{-1} l cm^{-1}).

and species like $ClRe(CO)_3$(2,2'-bipyridine) convince us that a mechanism other than nucleophilic substitution of the halide by the $M(CO)_5^-$ must be responsible for the net reaction of $XM(CO)_3L$ and $M(CO)_5^-$. It is possible that the key step in the reaction is in fact the reduction of $XM(CO)_3L$ by $M(CO)_5^-$. To determine the energetic feasibility of this possibility we measured the reduction $E_{1/2}$ (vs. SCE) values for pertinent substances, Table 2. The data in Table 2 show that the $XRe(CO)_3L$ complexes which are most easily reduced are just the ones that react with $Re(CO)_5^-$ to give the $Re_2(CO)_8L$ products. The non-reactive complexes, $ClRe(CO)_3(pyridine)_2$, $ClRe(CO)_3$(diars), and $ClRe(CO)_3$(2-phos), are all more difficult to reduce than $Re_2(CO)_{10}$ while the reactive complexes are more easily reduced. These data suggest that $Re(CO)_5^-$ is a strong enough reducing agent to reduce the reactive $XM(CO)_3L$ complexes. Some ambiguity is introduced because the reduction potential for $Re_2(CO)_{10}$ may not exactly reflect the reducing power of the mononuclear $Re(CO)_5^-$. We do see, though, that it is easier to reduce $Mn_2(CO)_{10}$ than $Re_2(CO)_{10}$, and this correlates with the lack of observable reaction of $Mn(CO)_5^-$ with $ClRe(CO)_3$(1,10-phenanthroline).

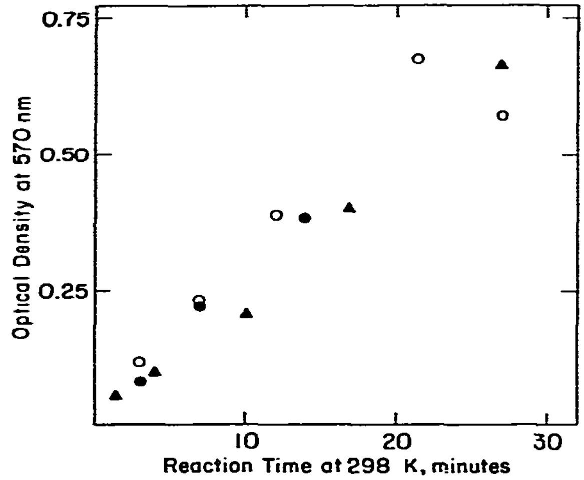

Fig. 2. Plot of optical density at 570 nm as a function of reaction time for THF solution of 5×10^{-3} *M* $Re(CO)_5^-$ and 4.3×10^{-4} *M* $XRe(CO)_3$(1,10-phenanthroline) (X = Cl (○); Br (●); and I (▲)). Cell pathlength is 1.0 cm, and the final product is $Re_2(CO)_8$(1,10-phenanthroline). The molar absorptivity at 570 nm is 2670 $mol^{-1}\ l\ cm^{-1}$.

c. Proposed mechanism for $M_2(CO)_8L$ formation. The energetic feasibility of reaction 2 does not by itself prove that it is at all important in the overall reaction indicated in reaction 1. However, the lack of reaction of $ClRe(CO)_3(pyridine)_2$ and $Re(CO)_5^-$, even at elevated temperatures, suggests that simple nucleophilic displacement of Cl^- cannot account for the chemistry in reaction 1. We thus offer

$$Re(CO)_5^- + ClRe(CO)_3(1{,}10\text{-phenanthroline}) \rightarrow [Re(CO)_5 + ClRe(CO)_3(1{,}10\text{-phenanthroline})^-] \qquad (2)$$

TABLE 2

REDUCTION POTENTIALS FOR PERTINENT MOLECULES

Compound	$E_{1/2}$ vs. SCE(V) [a]
$ClRe(CO)_3$(1,10-phenanthroline)	−1.20
$IRe(CO)_3$(1,10-phenanthroline)	−1.03
$ClRe(CO)_3$(2,2′-bipyridine)	−1.46
$ClRe(CO)_3(pyridine)_2$	−2.04
$ClRe(CO)_3$(diars)	−2.42
$ClRe(CO)_3$(2-phos)	−2.10
$Re_2(CO)_{10}$	−1.73 [b]
$Mn_2(CO)_{10}$	−1.06 [b]
1,10-Phenanthroline	−2.12 [c]
2,2′-Bipyridine	−2.24 [c]
Pyridine	−2.81 [c]
2,2′-Biquinoline	−1.82 [c]

[a] DME solution, Ar-purged, 0.1 *M* $[n\text{-}Bu_4N]ClO_4$ supporting electrolyte at 25°C. [b] These are the most recent values in propylene carbonate with 0.05 *M* $[Et_4N]Br$ [10]. [c] In 0.1 *M* $[n\text{-}Bu_4N]I$/DMF solution [11].

reaction 2 as a logical first step in the mechanism of reaction 1.

Subsequent formation of the final product may occur by concerted formation of a Re—Re bond and loss of Cl^- or by discrete loss of Cl^- followed by Re—Re bond formation. In any event, any mechanism involving free $Re(CO)_5$ or $Re(CO)_3$(1,10-phenanthroline) 17-electron radicals can be ruled out, since $Re_2(CO)_8$(1,10-phenanthroline) formation is not accompanied by formation of $Re_2(CO)_{10}$ or $Re_2(CO)_6$(1,10-phenanthroline)$_2$. The $Re_2(CO)_{10}$ and $Re_2(CO)_6$(1,10-phenanthroline) are known products [2] from the coupling of $Re(CO)_5$ and $Re(CO)_3$(1,10-phenanthroline) radicals, respectively.

Other than the correlation of reactivity with ease of reduction of the $XM(CO)_3L$ species, we have no evidence for the suggested pathway in reaction 2. We do, however, have ample precedence for our proposal from work of Dessy and Weissman [5]. Also, the lability of the halide in the one-electron reduced $XM(CO)_3L$ species is consistent with the fact that reduction of $XM(CO)_5$ yields X^- and $M(CO)_5^-$ in a two-electron process [6]. Likewise, preliminary results in our laboratory show facile loss of halide from $XM(CO)_3L$ upon Na/Hg or electrochemical reduction of $XM(CO)_3L$ which yields X^- and $M(CO)_3L^-$. We have not succeeded in isolating or observing the one-electron reduced species $XM(CO)_3L^{\cdot}$.

Experimental section

Materials. $M_2(CO)_{10}$ (M = Mn, Re) and $XM(CO)_5$ (X = Cl, Br for M = Re, and X = Br for M = Mn) were all obtained from Pressure Chemical Co. All ligands used are commercially available. The $IRe(CO)_5$ was prepared by UV-irradiation of $Re_2(CO)_{10}$ in N_2-purged solution of I_2 in isooctane followed by chromatography on alumina for purification [7]. All derivatives of $XM(CO)_5$ were prepared by heating isooctane solutions of $XM(CO)_5$ in the presence of the ligand followed by chromatography and recrystallization from CH_2Cl_2 by addition of n-pentane [8]. All compounds were identified by their infrared spectrum in the CO stretching region: for $XM(CO)_3L$ bands near 2020, 1915, 1890 cm^{-1} are found. The infrared stretching frequencies for most of these complexes are given in ref. 8. The THF solutions of $M(CO)_5^-$ were prepared by Na/Hg reduction of $M_2(CO)_{10}$ [9].

The THF solvent used for preparation and reaction of $M(CO)_5^-$ was distilled from Na/benzophenone under Ar. The DME electrochemical solvent was distilled from $LiAlH_4$ under Ar. The polarographic quality $[n\text{-}Bu_4N]ClO_4$ was obtained from Matheson.

Synthesis and characterization of $M_2(CO)_8L$ complexes. The metal—metal bonded complexes resulting from the interaction of $M(CO)_5^-$ and $XM(CO)_3L$ (L = 2,2′-bipyridine, 1,10-phenanthroline, 2,2′-biquinoline, and 4,7-diphenyl-1,10-phenanthroline) all have very similar properties. We outline the synthesis and characterization of $Re_2(CO)_8$(1,10-phenanthroline), since it is representative.

Synthesis of $Re_2(CO)_8$(1,10-phenanthroline) was by airless addition (in the dark) of a tetrahydrofuran solution of $NaRe(CO)_5$ [9] to a deoxygenated $ClRe(CO)_3$(1,10-phenanthroline) solution. The net displacement of Cl^- by $Re(CO)_5^-$ occurs rapidly at 25°C to yield a highly colored solution containing the desired complex and NaCl precipitate. The colored solution was decanted and reduced in volume by rotary evaporation. The $Re_2(CO)_8$(1,10-phenanthroline) was purified by column chromatography on alumina, recrystallization from CH_2Cl_2 by addition of n-pentane, and sublimation, it is a red-purple solid which gives a satisfactory elementary analysis: Found: C, 30.70, H, 1.03, N, 3.74. $C_{20}H_8N_2O_8Re$ calcd.: C, 30.9; H, 1.03; N, 3.60%. The m.p. is 252—254°C (corrected), and the complex has strong IR bands in the CO stretching region at 2075, 1993, 1900, and 1885 cm^{-1} in $CHCl_3$. The lowest electronic absorption band position is very solvent sensitive and falls at 516 nm (ϵ 7900 mol^{-1} l cm^{-1}) in THF. In CH_2Cl_2 the electronic absorption bands are at 527 (0.21); 350 (sh) (0.27); 290 (sh) (0.64) and 267 nm (0.93) where the numbers in parentheses are the relative absorbance. The band at 267 nm is the characteristic 1,10-phenanthroline intraligand absorption with an absorbance consistent with one 1,10-phenanthroline unit per molecule.

The other $M_2(CO)_8L$ complexes were prepared using a similar procedure and were characterized spectroscopically in the IR and UV-vis. Additionally, since the relative rates were measured in THF, the position and intensity of the lowest band was measured in THF: $Re_2(CO)_8$(2,2'-biquinoline), λ_{max} 660 nm (ϵ 6200 mol^{-1} l cm^{-1}); $Re_2(CO)_8$(4,7-diphenyl-1,10-phenanthroline), λ_{max} 532 nm (ϵ 9900 mol^{-1} l cm^{-1}). These complexes were prepared from reaction of $Re(CO)_5^-$ with $ClRe(CO)_3L$. Infrared spectral features for these $Re_2(CO)_8L$ complexes in $CHCl_3$ include five strong CO stretching absorptions analogous to the prototype $Re_2(CO)_8$(1,10-phenanthroline): $Re_2(CO)_8$(2,2'-biquinoline), 2076, 1987, 1970, 1895, 1885 cm^{-1}; $Re_2(CO)_8$(4,7-diphenyl-1,10-phenanthroline), 2073, 1991, 1961, 1896, 1885 cm^{-1}; $Re_2(CO)_8$(2,2'-bipyridine), 2074, 1990, 1960, 1897, 1885 cm^{-1}. Electronic absorption spectra were recorded in CH_2Cl_2 and band maxima and relative absorbance in parentheses are given: $Re_2(CO)_8$(4,7-diphenyl-1,10-phenanthroline), 538 (0.15); 350 (sh) (0.20), 280 nm (0.66); $Re_2(CO)_8$(2,2'-biquinoline), 668 (0.10), 460 (0.12), 368 (0.52); 353 (0.48), 295 (sh) (0.47), 268 nm (0.98).

Reaction of $Re(CO)_5^-$ with $BrMn(CO)_3$(1,10-phenanthroline) yields $Re(CO)_5$-$Mn(CO)_3$(1,10-phenanthroline) with a lowest absorption maximum at 563 nm (ϵ 4950 mol^{-1} l cm^{-1}) in THF. The complex exhibits five strong CO stretching absorptions in $CHCl_3$ at 2076, 1977, 1966, 1895, 1882 cm^{-1}, and electronic absorptions in CH_2Cl_2 at 570 (0.19); 425 (sh) (0.16); 340 (sh) (0.25); 290 (sh) (0.45) and 268 nm (0.86), where the numbers in parentheses represent relative absorbance.

For compounds of the type $M_2(CO)_8L$, where elemental analyses were not obtained, the purity was established by demonstrating that near-UV irradiation in the presence of CCl_4 quantitatively yields the corresponding mononuclear $M(CO)_5Cl$ and $ClM(CO)_3L$ complexes as compared to authentic samples. The photochemistry procedures are described in ref. 2.

Relative rate studies. Relative rates for reaction of $Re(CO)_5^-$ with $XM(CO)_3L$ were determined by adding a THF solution of $Re(CO)_5^-$ to a THF solution of $XM(CO)_3L$ under Ar. The initial $Re(CO)_5^-$ and $XM(CO)_3L$ concentrations in the reacting solution were 5×10^{-3} *M* and 4.3×10^{-4} *M* respectively. Product formation was monitored as a function of time by measuring the visible spectral changes accompanying the generation of $Re(CO)_5$—$M(CO)_3L$, cf. Fig. 1 and 2. The reactions were followed to completion, and the plots of optical density of product against time were linear to >20% conversion. "No reaction" entries in Table 1 have been made for systems where $XM(CO)_3L$, $XM(CO)_3L_2$ could be recovered unchanged from solutions containing $M(CO)_5^-$.

Polarography. DC polarography was run using a PAR174A Polarographic Analyzer with a two compartment cell. A dropping Hg working electrode was used with a Hg counter electrode and a saturated calomel electrode (SCE) was the reference electrode. The cell was purged with Ar prior to use and remained under Ar for the polarographic studies. The complexes were run at $\sim 2 \times 10^{-3}$ *M* and the supporting electrolyte was a 0.1 *M* $[n\text{-}Bu_4N]ClO_4$ in DME.

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