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Formation of Oxometal Complexes by the Oxidative Decarbonylation of Metal Carbonyls

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Abstract

Various metal carbonyls are readily decarbonylated by oxidation with tert-butyl hydroperoxide in benzene or dichloromethane solutions either at ambient temperatures or by slight heating. With the tri-carbonyl complex (dien)Mo$(CO)_3$, the oxidative decarbonylation affords the trioxo complex (dien)MoO_3 in high yields. The rhenium tricarbonyl Cp*Re$(CO)_3$ is analogously converted by tert-butyl hydroperoxide in a one-step procedure to the trioxo complex Cp*ReO_3, either by heating a benzene solution to 80 °C or by actinic irradiation at 25 °C. The products derived from the oxidative decarbonylation of the other metal carbonyls have not been as readily identified since the corresponding oxometal complexes are by and large structurally uncharacterized.

Introduction

Metal carbonyls are subject to decarbonylation by such oxygen-atom donors as [O] = amine oxides, sulfoxides, iodoxides, etc. which promote ligand loss by the oxidative elimination of carbon dioxide [1–7]. The resulting metal fragment, being coordinatively unsaturated, undergoes a subsequent rapid ligation by a variety of added nucleophiles (L). Thus for a representative oxygen-atom donor such as $[O] = (CH_3)_3NO$ the overall stoichiometry for CO_2 loss in eqn. (1) is tantamount to ligand substitution of the metal carbonyl, where L = phosphines, phosphites, amines, nitriles, olefins, etc. [8–10].

$$\text{(Metal)CO} + (CH_3)_3NO + L \longrightarrow \text{(Metal)L} + (CH_3)_3N + CO_2 \qquad (1)$$

Although the synthetic utility of the oxidative ligation [11] in eqn. (1) has been largely restricted to uncharged nucleophiles, its application to carbonyl replacement with anionic ligands would be highly desirable. Indeed the direct conversion of a carbonylmetal to an oxometal, i.e.

$$\text{(Metal)CO} \xrightarrow{[O]} \text{(Metal)=O} + CO_2 \qquad (2)$$

is particularly relevant owing to the increased interest in a variety of metal-centered oxygen transfer reactions [12, 13]. The recent use of hydrogen peroxide in a two-phase benzene/water solvent system for the oxidative conversion of the tricarbonylrhenium complex Cp*Re$(CO)_3$ to the corresponding trioxo derivative in one-step [14], suggests that peroxides may be effective oxygen-atom donors for the oxidative ligation in eqn. (2). Among the various types of peroxides extant [15], tert-butyl hydroperoxide (TBHP) appeared to be an especially desirable reagent owing to its ready availability and solubility in organic solvents [16]. Accordingly in this study, we first established its efficacy in the preparation of Cp*ReO_3 and then its applicability to various types of other carbonyl–metal complexes.

Experimental

Materials

tert-Butyl hydroperoxide (TBHP, Wallace and Tiernan, 87%) was purified by conversion to its sodium salt with 50% NaOH [17, 18], followed by neutralization with carbon dioxide and distillation *in vacuo*; boiling point (b.p.) 36 °C (15 mm). Molecular weight: calc. for $C_4H_{10}O_2$, 90.12; found [19], 90.7. The metal carbonyls $C_5(CH_3)_5Re(CO)_3$ [20], (dien)Mo$(CO)_3$ [21] where dien = diethylenetriamine, $[C_5(CH_3)_5Mo(CO)_2]_2$ [22], $C_5(CH_3)_5Fe(CO)_2I$ (ν(CO) = 2019 and 1971 cm^{-1}) [23], $Mo(S_2CNEt_2)_2(CO)_2$ [24], $[C_5(CH_3)_5Fe(CO)_2]_2$ (ν(CO) = 1929 and 1761 cm^{-1}) [25], $C_5(CH_3)H_4Mn(CO)_2(py)$ [26], (dien)Cr$(CO)_3$ [21], and $Mo(CO)_2(bpy)_2$ [27, 28] were prepared according to the reported procedures. Authentic samples of the possible oxometal products $C_5(CH_3)_5ReO_3$ [20], $Mo(S_2CNEt_2)_2O_2$ [29] and (dien)MoO_3 [30] were also prepared for comparative purposes by the procedures reported in the literature.

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TABLE 1. Oxidative decarbonylation of tricarbonylrhenium[a]

TBHP (eq.)[b]	Solvent	Additive[c] (eq.)[b]	Time (min)	Cp^*ReO_3 (%)[b]	$Cp^*Re(CO)_3$ (%)[d]
6	C_6H_6		10	36	30
6	C_6H_6[e]		10	27	30
6	C_6H_6	TsOH (0.5)	5	31	23
6	CH_2Cl_2		10^3	f	
6	C_6H_6	DBMP (0.5)	120	29[g]	23
10	C_6H_6	py (1.0)	250	7	70
10	C_6H_6	DBMP (1.0)	250	37[h]	9
6	C_6H_6	pyO (1.0)	400		92

[a] With 0.10 g (0.25 mmol) of $Cp^*Re(CO)_3$ in 10 ml solvent at 80 °C, unless indicated otherwise. [b] Relative to $Cp^*Re(CO)_3$ charged. [c] TsOH = *p*-toluenesulfonic acid, DBMP = 2,6-di-tertbutyl-4-methylpyridine, py = pyridine, pyO = pyridine *N*-oxide. [d] By IR absorbance at 2014 and 1923 cm^{-1}. [e] Unpurified (87%). [f] At 25 °C to afford black oil. [g] Also contains Bu_2pyH^+-ReO_4^- (37%). [h] $Bu_2pyH^+ReO_4^-$ (43%).

Thermal Oxidative Decarbonylation of $C_5(CH_3)_5Re(CO)_3$

In a typical procedure, $Cp^*Re(CO)_3$ (0.10 g, 0.25 mmol) was dissolved in 10 ml of benzene together with 1.48 mmol (152 μl) of tert-butyl hydroperoxide (TBHP) to afford a colorless solution. No change was apparent at room temperature for 90 min, whereupon the solution was heated to reflux for 10 min. The color of the solution turned progressively yellow to orange and a small amount of brown precipitate formed. After filtration, the solution was reduced in volume to ~2 ml *in vacuo*, and 20 ml of hexane added. On cooling the mixture in an ice-water bath, yellow crystals of Cp^*ReO_3 formed. Yield, 33 mg (37%). The concentration of the mother liquor yielded 74 μmol (30%) of recovered $Cp^*Re(CO)_3$. The effects of acid (*p*-toluenesulfonic acid), base (2,6-di-tert-butylpyridine, pyridine), added ligand (pyridine *N*-oxide) and solvent (dichloromethane) on the oxidative decarbonylation of $Cp^*Re(CO)_3$ are listed in Table 1.

Photochemical Oxidative Decarbonylation of $C_5(CH_3)_5Re(CO)_3$

The oxidative decarbonylation of $Cp^*Re(CO)_3$ with TBHP was also carried out photochemically with the output from a 500-watt mercury lamp (Osram HBO 500 W/2) at 25 °C. Figure 1 shows the UV absorption spectrum of the tricarbonyl $Cp^*Re(CO)_3$ with $\lambda_{max} = 274$ nm ($\epsilon = 2800$ M^{-1} cm^{-1}). Similarly the UV–Vis absorption spectrum of the trioxo product Cp^*ReO_3 is shown in the Figure as the dashed curve with the red-shifted band at $\lambda_{max} = 299$ nm ($\epsilon = 5300$ M^{-1} cm^{-1}) together with a weaker, partially resolved band with a shoulder at $\lambda = 400$ nm ($\epsilon = 1000$ M^{-1} cm^{-1}). The spectral changes accompanying the actinic irradiation of 4.4×10^{-4} M $Cp^*Re(CO)_3$ in dichloromethane containing 1.7×10^{-2} M tert-butyl hydroperoxide are shown in Fig. 2. The temporal change in the absorption spectrum of the solution from that of $Cp^*Re(CO)_3$ to that of Cp^*ReO_3 was quantitatively evaluated at the monitoring wavelength of 400 nm. The maximum conversion of $Cp^*Re(CO)_3$ to the trioxo product (64%) was attained at ~25 min, but further irradiation led to a slower decomposition of Cp^*ReO_3 (Fig. 3, $t > 25$ min).

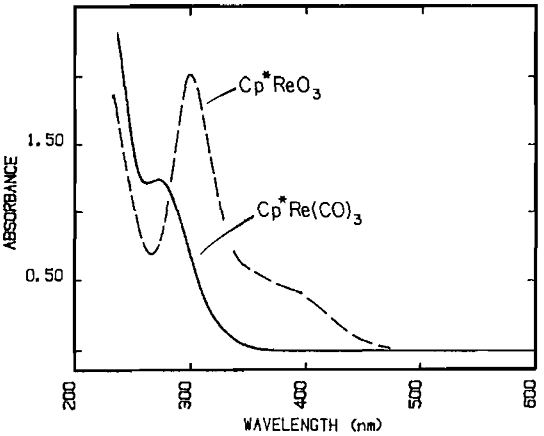

Fig. 1. Absorption spectrum of 4.4×10^{-4} M $Cp^*Re(CO)_3$ in dichloromethane. Dashed curve represents 3.8×10^{-4} M Cp^*ReO_3.

Thermal Oxidative Decarbonylations of Carbonylmetal Derivatives

Various carbonylmetal derivatives were thermally treated with TBHP as follows.

(dien)Mo(CO)$_3$

A weighed amount (0.17 g, 0.60 mmol) of (dien)-$Mo(CO)_3$ was suspended in 10 ml of dichloromethane containing 3.60 mmol (370 μl) of TBHP. The mixture was stirred in the dark for 20 h during which time a

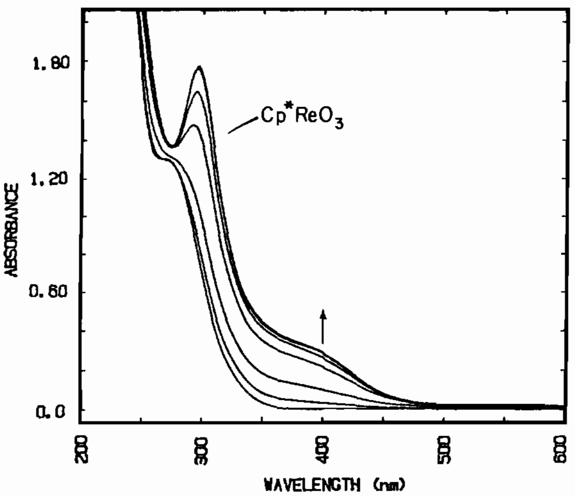

Fig. 2. Temporal change in the absorption spectrum of 4.4 × 10^{-4} M $Cp^*Re(CO)_3$ in dichloromethane containing 1.6 × 10^{-2} M TBHP under constant actinic irradiation for (bottom-to-top) 0, 5, 10, 15 and 5 min intervals.

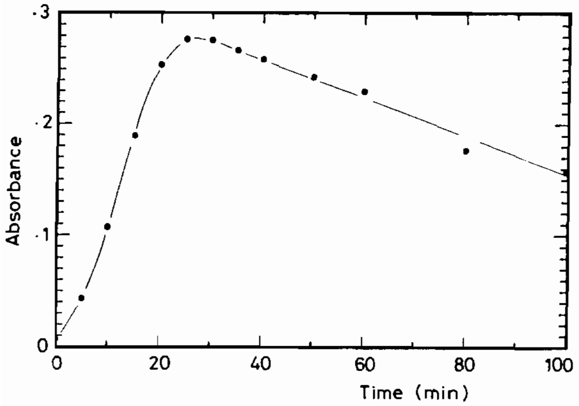

Fig. 3. Formation of Cp^*ReO_3 (as in Fig. 2) by following the absorbance change at 400 nm and subsequent decomposition upon continued irradiation. [Note absorbance of 0.28 corresponds to 62% conversion to Cp^*ReO_3.]

cream-colored solid precipitated and 53 ml of gas (2.3 mmol, 3.9 eq. based on Mo) was liberated. The off-white solid was dissolved in 6 ml of water, and the solution filtered. Addition of 100 ml of ethanol, and cooling the solution in an ice bath yielded 0.14 g (90%) of (dien)MoO_3 as colorless microcrystals, the IR spectrum of which was identical to an authentic sample prepared from MoO_3 and dien [30].

(dien)Cr(CO)$_3$

A solution of 0.63 mmol (0.15 g) of (dien)Cr$(CO)_3$ in 10 ml of dichloromethane containing 3.8 mmol (385 μl) of TBHP rapidly evolved 1.6 mmol (2.6 eq.) of gas, and it led to a red–brown precipitate showing IR bands at 3241, 3142 and 905 cm^{-1} similar to those at 3248, 3125 and 842 cm^{-1} in the trioxo complex (dien)MoO_3 from the related tricarbonylmolybdenum complex (*vide supra*).

$[C_5(CH_3)_5Mo(CO)_2]_2$

A solution of 0.15 g (0.26 mmol) of $[Cp^*Mo(CO)_2]_2$ in 10 ml of benzene containing 2.1 mmol of TBHP showed no change at room temperature for 30 min. When the solution was refluxed for 50 min, it turned black. Chromatography on silica gel successively with hexane/dichloromethane (1:1), dichloromethane and ethyl acetate yielded traces (~5 mg) each of orange, pale yellow and yellow residues. No reactant was apparent, and the preponderant product consisted of a black colloidal solid.

$C_5(CH_3)_5Fe(CO)_2I$

A deep red solution of 0.24 mmol (90 mg) of $Cp^*Fe(CO)_2I$ in 10 ml of dichloromethane containing 4 eq. of THBP was stirred at 25 °C for 4 h. IR analysis showed no change in the intensity of the carbonyl bands at 2019 and 1971 cm^{-1}. Addition of 0.96 mmol (0.17 g) *n*-chloroperbenzoic acid caused the solution to bubble vigorously. The IR analysis of the clear red solution showed only traces of $Cp^*Fe(CO)_2I$. Workup of the reaction mixture yielded a red compound tentatively assigned as Cp^*_2Fe.

$C_5H_4(CH_3)Mn(CO)_2(py)$

The bright orange solution of 0.37 mmol (0.10 g) of $MeCpMn(CO)_2py$ and 1.5 mmol (152 μl) of TBHP rapidly evolved gas. The IR spectrum (KBr) of the brown precipitate was consistent with that of manganese dioxide.

$Mo(S_2CNEt_2)_2(CO)_2$

A suspension of 0.33 mmol (0.15 g) of $Mo(S_2CNEt_2)_2(CO)_2$ in 10 ml of dichloromethane containing 1.34 mmol of TBHP at −15 °C smoothly evolved 0.6 mmol (13.5 ml) of gas. Removal of the solvent *in vacuo* afforded a yellow–green oil which upon extraction with 5 ml of dichloromethane yielded 37 mg of a yellow solid. Comparison of the IR spectrum with that of $Mo(S_2CNEt_2)_2O_2$ indicated complete oxidative decarbonylation to a different compound [29].

$[C_5(CH_3)_5Fe(CO)_2]_2$

A solution of 0.3 mmol (0.15 g) of $[Cp^*Fe(CO)_2]_2$ in 10 ml of dichloromethane containing 1.21 mmol of TBHP showed no change at room temperature for 30 min. Furthermore, IR analysis of the mixture after refluxing it for 20 h showed the unchanged principal carbonyl bands of $Cp^*Fe(CO)_2I$ at 1929 and 1761 cm^{-1}. A pair of weak bands at 2028 and 1978 cm^{-1} was attributed to a minor product, since TLC analysis showed the reactant to be the major component of the reaction mixture.

Results and Discussion

The oxidative decarbonylation of a metal carbonyl to an oxometal complex according to the stoichiometry in eqn. (2) represents a formal four-electron change. As such, when tert-butyl hydroperoxide is employed as the oxygen-atom donor, two moles are required for the decarbonylation of each carbonyl ligand. Thus for the oxidative conversion of (dien)-Mo(CO)$_3$ to the trioxo derivative, the stoichiometry will be

$$\text{(dien)Mo(CO)}_3 + 6\text{tBuOOH} \longrightarrow \text{(dien)MoO}_3 + 3\text{CO}_2 + 6\text{tBuOH} \qquad (3)$$

A similar stoichiometry is expected for the conversion of tricarbonylrhenium complex Cp*Re(CO)$_3$ in Table 1, although we were unable to attain sufficiently high yields of the trioxo derivative to test this stoichiometry thoroughly. Part of the deficiency was undoubtedly caused by the competitive destruction of Cp*ReO$_3$ by the hydroperoxide. The latter is readily shown in Fig. 3 by the continued disappearance of the trioxo derivative after its concentration has reached a maximum value.

The oxidative conversion of three carbonyl ligands according to eqn. (3) undoubtedly proceeds by a multi-step sequence of intermediates since it represents an overall twelve-electron change. As such, the putative mono- and di-oxo intermediates must each be converted further with high efficiencies. It is thus all the more remarkable that trioxomolybdenum product (dien)MoO$_3$ can be isolated in yields exceeding 90% from the tricarbonyl precursor (dien)Mo-(CO)$_3$ in a one-step process. Furthermore the formation of Cp*ReO$_3$ from the tricarbonyl precursor in Table 1 by the same one-step procedure is noteworthy.

The ready characterization of the oxometal products (dien)MoO$_3$ and Cp*ReO$_3$ has undoubtedly facilitated the delination of the oxidative decarbonylation induced by tert-butyl hydroperoxides. Unfortunately, the same situation did not apply to the other carbonylmetals examined in this study, especially those for which the terminal oxometal complex has not been structurally characterized – as in the case of the bridging oxo ligands [31, 32]. The possibility that oxidative decarbonylation can lead to μ-oxometals [33] rather than terminal oxometals detracts from their desirability in metal-centered oxygen transfer reactions [13]. Nonetheless the rapid reactions observed in these studies have shown that a wide variety of carbonylmetals are subject to oxidative decarbonylation by TBHP. With most carbonylmetals, the thermal reactions with the peroxide were unfortunately too difficult to regulate without an attendant destruction of the remaining ligands. It is clear that further detailed studies of the precise reaction conditions are needed to control the selective formation of the desired oxometal derivatives. To this end, the preliminary photochemical studies of the kind shown in Fig. 2 will hopefully provide the means to effect such a high selectivity.

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