Preliminary communication

SUBSTITUTION MECHANISMS AT METAL CARBONYL CENTERS; CONVERSION OF Ph₃P(CO)₄ReBr TO Ph₃P(CO)₄ReCH₃ VIA AN ANIONIC ACYL INTERMEDIATE

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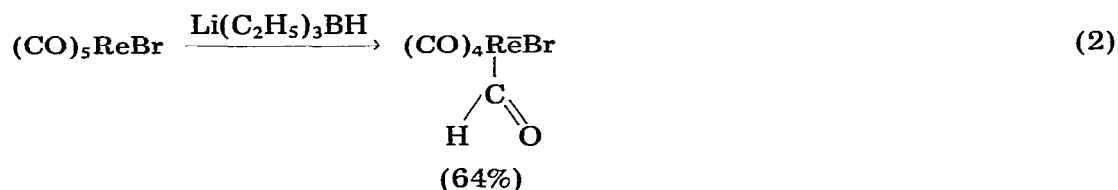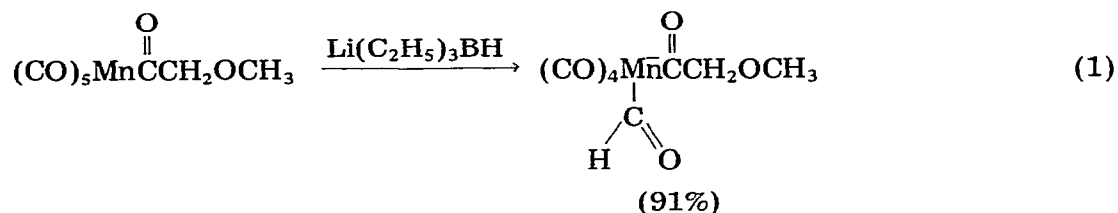
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Summary

The substitution reaction $Ph_3P(CO)_4ReBr + CH_3Li \rightarrow Ph_3P(CO)_4ReCH_3$ is shown to occur by initial CH_3Li attack upon coordinated CO.
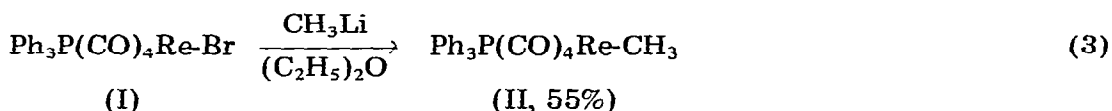

There are numerous substitution reactions in which one unidentate ligand replaces another at a transition metal center. As outlined in current textbooks [1,2], most of these fall into two basic mechanistic categories: associative (A or I_a) and dissociative (D or I_d).

Over the past several years, a variety of new reactions involving nucleophilic attack at coordinated CO have been discovered [3—5]. For instance, in the course of our studies on the synthesis of transition metal-formyl complexes [6,7], we observed that trialkylborohydrides attacked a variety of metal carbonyl complexes at coordinated CO in preference to other electrophilic sites. Two such reactions are depicted in eq. 1 and eq. 2 [7]. The latter has also been reported by Lukehart [8]. The absence of any reactions involving the acyl, ether, and bromide groups in eq. 1, 2 is noteworthy.

$$(CO)_5Mn\overset{\overset{\text{O}}{\|}}{C}CH_2OCH_3 \xrightarrow{\text{Li(C}_2\text{H}_5)_3\text{BH}} (CO)_4Mn\overset{\overset{\text{O}}{\|}}{\underset{\underset{H}{\overset{}{\underset{}{C}}}\diagdown O}{C}}CH_2OCH_3 \qquad (1)$$

(91%)

$$(CO)_5ReBr \xrightarrow{\text{Li(C}_2\text{H}_5)_3\text{BH}} (CO)_4\underset{\underset{H}{\overset{}{\underset{}{C}}\diagdown O}}{\overline{Re}}Br \qquad (2)$$

(64%)

These observations led us to consider that certain nucleophilic substitution reactions at metal carbonyl centers might proceed via initial attack at coordinated CO. Alkyl- and aryl-metals such as $(\eta\text{-}C_5H_5)Fe(CO)(PPh_3)R$ [9], $Ar_3P(CO)_4ReR$ [10], and $[(CO)_5WR]^-$ [11] have been synthesized by the reaction of organo-lithium reagents with the corresponding metal carbonyl iodides or bromides. We selected the reaction depicted in eq. 3, originally reported by Kaesz and McKinney [10], for initial study.

$$Ph_3P(CO)_4Re\text{-}Br \xrightarrow[\text{(C}_2\text{H}_5)_2\text{O}]{CH_3Li} Ph_3P(CO)_4Re\text{-}CH_3 \qquad (3)$$
$$\text{(I)} \qquad\qquad\qquad \text{(II, 55\%)}$$

A solution of I (ca. 0.03 M) in THF at $-78°C$ was treated with 1.5 equiv of CH_3Li in ethyl ether. The solution was warmed to room temperature, and an IR spectrum was recorded. No absorptions due to I or II (eq. 3) were present. The spectrum consisted of bands at 2011s, 1917s, 1875s, and 1536m cm^{-1}. Heating this solution at 50°C for 5 h caused a white precipitate to form. The IR spectrum of the supernate indicated II to be the only metal carbonyl species in solution. The white precipitate was isolated and gave a positive $AgNO_3$ test, as would be expected of LiBr.

A solution of I in THF-d_8 (ca. 0.37 M, containing p-di-t-butylbenzene standard) in a ^1H NMR tube at $-54°C$ was treated with 1.0 equiv. of CH_3Li in THF-d_8. A new ^1H NMR resonance appeared immediately at δ 2.27 ppm. Integration of the spectrum indicated an 88% yield of this intermediate (assuming a 3H resonance). At 55°C, the intermediate disappeared while II appeared ($\delta -0.46$ ppm, d, J 8 Hz). These processes followed the same rate law:

$$\frac{-d[\text{intermediate}]}{dt} = \frac{d[\text{II}]}{dt} = k_{obs}[\text{intermediate}]$$

From data collected over 2 half lifes at 55°C, k_{obs} was determined to be 1.10×10^{-4} sec^{-1}.

The above observations clearly establish that an intermediate is generated under conditions for the conversion of I to II. We propose the structure fac-Li$^+$ $[(CO)_3Re(COCH_3)(PPh_3)(Br)]^-$ (III, Scheme 1) for this species on the basis of its spectral properties. The IR $\nu(C=O)$ for the related acyl anion cis-Li$^+$ $[(CO)_4Re(COCH_3)Br]^-$ appears at 1565 cm^{-1} [8], and the $\nu(C\equiv O)$ values of III closely match those of the anionic octahedral rhenium tricarbonyl fac-$N(CH_3)_4^+$-$[(CO)_3Re(COCH_3)(COC_6H_5)(P(OCH_3)_3)]^-$ recently reported by Casey [12].

To further support our structural assignment, III was isolated by precipitation at 0°C with cold hexane. The resulting light yellow powder was washed with hexane and dried under vacuum at 0°C. A ^1H NMR spectrum at $-25°C$ in acetone-d_6 showed the expected resonances for III (δ 7.43 ppm, m, 15H; 2.23, s, 3H). Also present was THF (ca. 1.25 equiv), which commonly solvates Li$^+$ salts of organometallic anions [7b]. The ^{13}C NMR spectrum of isolated III ($-25°C$, acetone-d_6, ca. 0.02 M Cr(acac)$_3$) displayed acetyl (291.2, 52.3 ppm) and carbonyl (197.9, 196.6, 194.6 ppm) resonances comparable to those observed in other rhenium complexes [7b,13].
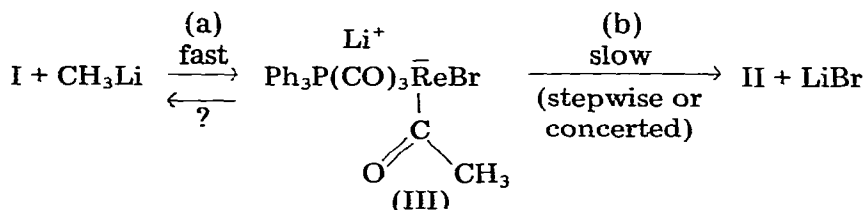
To rigorously establish that the conversion of I to II occurs via III, conven-

tional mechanisms must be probed. For instance, it is conceivable that III slowly reverts to starting materials, which then rapidly react by a conventional S_N2 (or other) mechanism. In such an event, the disappearance of III would still follow a first order rate law. To investigate this possibility, we carried out a crossover experiment.

Hence III was generated at $-60°C$ by adding 0.388 mmol of CH_3Li in ca. 0.45 ml of THF-d_8 to 0.388 mmol of I in ca. 0.45 ml of THF-d_8. A high amplitude ^1H NMR spectrum indicated that no CH_3Li remained. Isotopically labeled starting material, $[(C_6H_5)_2(C_6D_5)P](CO)_4ReBr$ (I-d_5; 0.392 mmol in ca. 0.35 ml THF-d_8) was then added. The reaction mixture was heated at $55°C$ for 24 h and the resulting II was isolated. Mass spectrometric analysis (M^+-CH_3 peak) indicated a ca. 82/18 ratio of II-d_0/II-d_5. A second experiment conducted on a 0.230 mmol scale afforded a ca. 77/23 ratio of II-d_0/II-d_5.

The preceding data require that $\gtrsim 60\%$ of the time, III decomposes to II by a path not involving the reversal of step (a), Scheme 1. The most probable decomposition path is depicted as step (b), Scheme 1. The operation of a minor second (simultaneous) mechanism for the formation of II, while not required by any of our data, cannot be excluded in view of the II-d_5 formed in the above experiment. However, since many label scrambling avenues can be formulated, such as partial reversal of step (a) on the time scale of the decomposition of III, followed by the rapid reformation of III, we believe that step (b) is the sole route by which II is formed.

SCHEME 1. Proposed principal substitution mechanism.

$$I + CH_3Li \underset{?}{\overset{\substack{(a)\\ fast}}{\rightleftarrows}} Ph_3P(CO)_3\bar{Re}Br \xrightarrow[\substack{(stepwise\ or\\ concerted)}]{\substack{(b)\\ slow}} II + LiBr$$

(with Li^+ above $Ph_3P(CO)_3\bar{Re}Br$, and below: $\underset{(III)}{\underset{O\diagup\diagdown CH_3}{\overset{\diagup\diagdown}{C}}}$)

A final point concerns the α-elimination of bromide from III (Scheme I). Two paths must be considered: (a) methyl migration concerted with Br$^-$ loss, and (b) dissociation of bromide to form yet another intermediate (coordinatively unsaturated or solvated), followed by methyl migration to the metal. The present data do not distinguish these possibilities, However, the microscopic reverse of this last step (i.e., II + LiBr → III) constitutes an example of a "CO insertion" reaction. These have been subjected to extensive mechanistic investigation [14]; conversions of alkylmanganese compounds such as $(CO)_5MnCH_3$ to acylmanganese compounds of the type $L(CO)_4Mn(COCH_3)$ (L = PPh$_3$, CO, I$^-$) have been well established as proceeding by a stepwise mechanism involving the coordinatively unsaturated intermediate $(CO)_4Mn(COCH_3)$ (and/or a solvate).

Mechanisms similar to the one depicted in Scheme 1 have been previously discussed in the literature. Certainly the oxidative removal of coordinated CO by $(CH_3)_3N^+$—O$^-$ [4,15], and Brunner's reactions of alkyoxycarbonyliron complexes with carbon nucleophiles [3] bear important conceptual relationships.

To account for the substitution kinetics of $Fe(NO)_2(CO)_2$ in THF, Basolo has proposed a mechanism featuring initial solvent attack at CO [16]. On the basis of rate data, Dobson has suggested that the halide-dependent component of the substitution reaction $(n\text{-}C_4H_9)_4N^+ X^- + Cr(CO)_6 \rightarrow (n\text{-}C_4H_9)_4N^+ [Cr(CO)_5X]^- + CO$ proceeds via initial attack of X^- (X = Cl, Br, I) upon coordinated CO [17]. The formation of $[(Ph_3P)_2N]^+ [W(CO)_5X]^-$ species from $W(CO)_6$ and $[(Ph_3P)_2N]^+ X^-$ has been proposed to proceed similarly [18]. However, direct observation of $[(CO)_5M(COX)]^-$ intermediates, and hence unequivocal mechanistic proof, has not proved possible in these reactions. Brown has perceptively noted that the attack of bases on coordinated CO in octahedral metal carbonyls can result in enhanced lability of cis-ligands [19]. Some of the substitution reactions surveyed by him [19] may proceed by mechanisms related to the one in Scheme 1.

In summary, this study has provided the first definitive proof that substitution of one unidentate ligand for another at a metal carbonyl center can proceed via initial attack at coordinated CO.

Acknowledgements

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