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Reactions of Transition Metal Carbonyls with Organolithium Compounds. II. Prediction of Nucleophilic Attack at Carbon and Resulting Stereochemistry[1]

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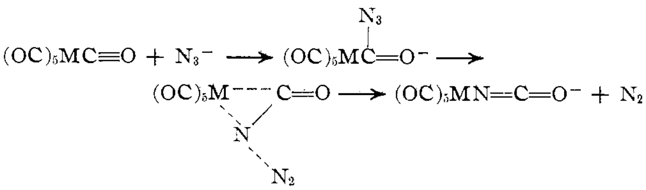
$Co(CO)_4M(C_6H_5)_3$ (M = Sn and Pb) and $Fe(CO)_4P(C_6H_5)_3$ are found to react with phenyllithium and methyllithium to yield stable *trans*-carbene complexes after ethylation. For metal carbonyls, it is proposed that there is a direct correlation between the apparent CO stretching force constant and the charge residing on the carbonyl carbon atom. The use of these force constants in predicting the reactivity at carbon by attacking nucleophiles is proposed. It is found that when there is a choice of carbonyl groups within a molecule, nucleophilic attack always occurs at the CO group with the greater stretching force constant. This proposal is substantiated by all known reactions of organolithium compounds with metal carbonyls.

Introduction

There are several reactions reported in the literature which indicate that metal carbonyls are susceptible to attack by nucleophiles. Among these are (a) the exchange of oxygen with $Re(CO)_6^+$ which is believed to occur by an attack on a carbon atom by H_2O or ^-OH to give intermediates of the type $(OC)_5ReC(OH)_2^+$ or $(OC)_5ReCOOH$, respectively,[2] (b) the reactions of $M(CO)_4L_2^+$ complexes (M = Mn, Re; L = $P(C_6H_5)_3$, 1,10-phenanthroline) with alkoxides (^-OR; R = CH_3, C_2H_5, C_5H_{11}, $CH_2C_6H_5$) leading to products of the type $M(CO)_3L_2COOR$,[3-5] (c) the reactions of $M(CO)_6$ (M = Cr, Mo, W) with tetraethylammonium azide to yield ionic products of the type $N(C_2H_5)_4[M(CO)_5NCO]$,[6,7] and (d) the addition of organolithium reagents to metal carbonyls to give addition products.[1,8-10]

A recent study of (c) has shown that these reactions obey an SN2 type mechanism as indicated by first-order kinetics in metal hexacarbonyl and $(C_2H_5)_4N^+N_3^-$ concentrations.[11] This is interpreted as suggesting a rate-determining attack of the azide anion at the carbonyl carbon atom



This mechanism is supported by (a) MO calculations of a large positive charge on the carbonyl carbon atoms in $M(CO)_6$ molecules and (b) the absence of formation of azido compounds $M(CO)_5N_3^-$.

Although no detailed investigations of the mechanisms of reactions a, b, or d have yet been made, it appears that these reactions can best be explained also by nucleophilic attack at the carbonyl carbon atom. This idea has previously been put forth by Caulton and Fenske[12] based on their estimates of "atomic charges" obtained from Mulliken population analysis in octahedral metal hexacarbonyls.

In this paper we wish to report some new reactions of organolithium reagents with substituted metal carbonyls of iron and cobalt and to suggest possible uses of apparent CO stretching force constants in predicting reactivity at the carbonyl carbon atom by attacking nucleophiles.

Experimental Section

All reactions were carried out in a pure nitrogen atmosphere.

$Co(CO)_4Sn(C_6H_5)_3$ and $Co(CO)_4Pb(C_6H_5)_3$ were prepared using Graham's procedure.[13] A mixture of $Fe(CO)_4P(C_6H_5)_3$ and *trans*-$Fe(CO)_3[P(C_6H_5)_3]_2$ was obtained from the reaction of $Fe_3(CO)_{12}$ and $P(C_6H_5)_3$.[14] Separation was effected by sublimation at 180°; the monosubstituted complex was obtained as the sublimate. *trans*-$Mo(CO)_4[P(C_6H_5)_3]_2$ was prepared by reaction of stoichiometric quantities of $P(C_6H_5)_3$ and $Mo(CO)_6$ in refluxing diglyme for 34 hr. The yellow solid obtained was used without purification. $(CH_3)_3C_6H_2Cr(CO)_3$ was prepared by the method of Nichols and Whiting[15] and purified by sublimation at 95°.

$(C_6H_5)_3SnCo(CO)_3C(OC_2H_5)C_6H_5$ was prepared from 1.26 g (2.56 mmol) of $(C_6H_5)_3SnCo(CO)_4$ in 25 ml of anhydrous ether and 2.0 ml of 1.91 *M* (3.82 mmol) phenyllithium added dropwise through a syringe. The reaction solution was stirred at ambient temperature for approximately 1 hr during which time yellow crystals settled out. The solvent was removed at reduced pressure and ethylation with $(C_2H_5)_3O^+BF_4^-$ was performed as described previously.[1] The resulting pentane extract was cooled in Dry Ice in order to isolate the product. The crystalline product was purified by recrystallization from pentane at −70° to yield a microcrystalline, air-stable, yellow compound (mp 122–124°). *Anal.* Calcd for $(C_6H_5)_3SnCo(CO)_3C(OC_2H_5)C_6H_5$: C, 57.54; H, 4.02; mol wt 627.12. Found: C, 57.27; H, 4.23; mol wt 620 (osmometric in benzene).

The analogous $(C_6H_5)_3PbCo(CO)_4$ and $(C_6H_5)_3PFe(CO)_4$ reactions were carried out at 0° and resulted in yellow crystalline products, upon cooling the pentane solutions at −70°, which were both thermally and air unstable. No further purification was attempted on these compounds.

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TABLE I

FORCE CONSTANTS, REACTIVITIES, AND STEREOCHEMISTRIES OF METAL CARBONYLS INVOLVED IN REACTIONS WITH NUCLEOPHILES

Metal carbonyl	Force constants[a]		Reactivity with organolithium reagents[b]	Stereochemistry of addn complex[c]	Ref[d]
	k_1	k_2			
$Cr(CO)_6$	16.49	16.49	Yes	...	35, (36)
$(C_6H_5)_3PCr(CO)_5$	15.51	15.85	Yes	*cis*	(1), 37
$(C_6H_5)_3AsCr(CO)_5$[e]	...	...	Yes	*cis*	37
$(C_6H_5)_3SbCr(CO)_5$[e]	...	...	Yes	*cis*	37
$(CH_3)_3C_6H_2Cr(CO)_3$	...	14.97	No	...	*f*
$Mo(CO)_6$	16.52	16.52	Yes	...	(20), 35
$(C_6H_5)_3PMo(CO)_5$	15.49	15.96	Yes	*cis*	(20), 37
$(C_6H_5)_5AsMo(CO)_5$	15.51	15.98	Yes	*cis*	(20), 37
$(C_6H_5)_3SbMo(CO)_5$	15.69	16.00	Yes	*cis*	(20), 37
trans-$[(C_6H_5)_3P]_2Mo(CO)_4$	...	15.28	No	...	(20), *f*
$W(CO)_6$	16.41	16.41	Yes	...	35, (36)
$(C_6H_5)_3PW(CO)_5$	15.57	15.89	Yes	*cis*	(22), 37
$(C_6H_5)_3AsW(CO)_5$[e]	...	...	Yes	*cis*	37
$(C_6H_5)_3SbW(CO)_5$[e]	...	...	Yes	*cis*	37
$Fe(CO)_5$	16.98	16.41	Yes	Unknown	38, (39)
$(C_6H_5)_3PFe(CO)_4$	16.22	15.74	Yes	*trans*	*f*
trans-$[(C_6H_5)_3P]_2Fe(CO)_3$	...	15.01	No	...	*f*
$(C_6H_5)_3SnCo(CO)_4$	17.10	16.46	Yes	*trans*	*f*
$(C_6H_5)_3PbCo(CO)_4$	16.97	16.42	Yes	*trans*	*f*
$Mn_2(CO)_{10}$	16.06	16.33	Yes	...	*f*, 40, (41)
$(C_5H_5)Mn(CO)_3$	15.81	...	Yes	...	(*f*), 35
$(C_5H_5)Re(CO)_3$	...	...	Yes	...	42,
$Ni(CO)_4$	17.14	...	Yes	...	39, 43 (39)
$[(C_6H_5)_3P]_3Ir(CO)H$	15.02	...	No	...	*f*

[a] k_1 is the axial CO force constant; k_2 is the equatorial force constant, where applicable. Force constants are expressed in mdyn/Å. [b] CH_3Li and/or C_6H_5Li are the organolithium reagents used here. [c] Stereochemistry about metal based on resulting carbene complex which has been shown in the several cases investigated to be the same as the original LiR–$M(CO)_y$ addition product. [d] Parentheses indicate force constant references. [e] Force constant values are unavailable for these derivatives; however frequencies are very similar to those for the $(C_6H_5)_3P$ derivatives in the respective cases. It is therefore expected that the force constants are very similar. [f] Work of the authors.

Infrared spectra in pentane solutions showed the presence of two bands of equal intensity in the CO stretching region. These are due to a splitting of the E band predicted for the *trans* structures, this effect being attributed to the large asymmetry of the carbene ligand. Analogous spectra are reported for compounds of the type *trans*-$(C_6H_5)_3SnCo(CO)_3PR_3$ by Bower and Stiddard.[16] The following carbonyl stretching frequencies were observed: $(C_6H_5)_3SnCo(CO)_3C(OC_2H_5)C_6H_5$, 1967 and 1955 cm^{-1}; $(C_6H_5)_3PbCo(CO)_3C(OC_2H_5)C_6H_5$, 1969 and 1956 cm^{-1}; $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$, 1913 and 1898 cm^{-1}; $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$, 1905 and 1897 cm^{-1}.

For the cases in Table I in which no reaction occurred between the various metal carbonyl compounds and alkyllithium reagents, the reactants were in contact at room temperature for prolonged periods (2–3 hr). In general, quantitative recovery of the metal carbonyl reactants was obtained.

Relationship between CO Force Constants and Charge on the Carbon Atom

Detailed semiempirical molecular orbital calculations on several metal carbonyls have shown the carbon atoms to be positively charged whereas the oxygen atoms are negatively charged. For example, the atomic charges calculated for carbon atoms in $Fe(CO)_5$ and $Ni(CO)_4$ are $+0.256$ and $+0.219$, respectively;[17] that for carbon in $Cr(CO)_6$ is $+0.20$ in Caulton and Fenske's calculations,[12] $+0.099$ in Schreiner and Brown's calculations,[17] and $+0.107$ in Carroll and McGlynn's calculations.[18]

As the σ donor strength of carbon monoxide increases, the apparent force constant of the CO stretching vibration increases.[19] A decrease in metal–carbonyl π bonding also causes an increase in the CO stretching force constant. Since the σ bond is formed from an unshared pair of electrons located on carbon, an increase in this donation will result in a decrease in electron density about the carbon atom. Similarly a removal of electronic charge through the metal–CO π bond leads to a decrease in electronic charge at the carbon atom. The coefficients of the $2p_\pi$ orbitals of C and O in the π^* orbital of CO are 0.967 and 0.621, respectively; the charge center (which relates to the squares of these coefficients) lies mostly on the carbon atom.[20] Both the σ and π mechanisms for removal of electronic charge from the carbonyl group therefore result in an increase in the positive charge on the carbon atom. Hence, *an increase in the apparent CO force constant, whether interpreted as being due to a decrease in metal–CO π bonding or to an increased strength in metal–CO σ bonding, implies more positive character to the carbonyl carbon atom.*

This is a very important conclusion since the disposition of the M–CO bonding between σ and π effects and their respective effects on the CO stretching frequencies

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and force constants are contentious.[20–31] It should however be pointed out here that there is no *a priori* reason for assuming that equal electronic charge from the carbon through either the σ or π mechanism results in the same effect on the apparent CO stretching force constant. This correlation between positive charge on the carbon atom is nevertheless clearly shown in the work of Carroll and McGlynn[18] where the positive charge on the carbon atom is found to decrease (+0.107, +0.021, and +0.017) while the force constants simultaneously decrease (16.49, 15.19, and 15.01) in $Cr(CO)_6$, $C_6H_6Cr(CO)_3$, and $NH_2C_6H_5Cr(CO)_3$, respectively.

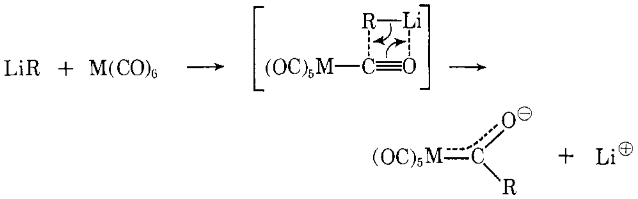
Prediction of Reactivity toward Nucleophiles

It therefore follows from the above discussion that the more reactive carbonyls toward attacking nucleophiles at carbon should be those with the larger CO force constants, assuming all other factors are equal. Likewise as the CO ligands are substituted by ligands which cause the force constants of remaining CO's to decrease, a simultaneous decrease in the positive charge on the carbon atom will occur. This will in turn lead to a decrease in reactivity at carbon toward nucleophilic attack.

It should be emphasized that we are attempting to relate a ground-state charge distribution to reactivity, a kinetic effect. Although it is possible to predict the behavior of reagents as the reaction starts, there is no way of ascertaining whether a sudden change in reaction path occurs as the reaction proceeds. However this seldom seems to be the case and predictions of this type have generally been very successful.[32]

We have established in Table I, for a group of metal carbonyls, their calculated CO force constants,[33–43] whether or not reaction occurs between them and LiR (R = CH_3 or C_6H_5), and the stereochemistry of the resulting compound where applicable.

Organolithium reagents as the attacking nucleophiles were the chosen examples because of the extensive work carried out on such reactions due to their role in the synthesis of alkoxycarbene-type ligands bonded to transition metals. Although the majority of the reactions of organolithium compounds with metal carbonyls appear to be too fast for convenient kinetic study, these reactions have qualitatively been shown to be dependent on both the nature of the lithium reagent as well as that of the metal carbonyl. An example of the assumed reaction pathway for the addition process is[44]



This scheme resembles the proposed mechanism for reactions of organolithium reagents with ketones which show a dependence in both RLi and the reagent undergoing attack.[45]

Table I indicates reaction to occur between LiR and MC≡O whenever $k > 15.3$. The exact partitioning between force constant values and reactivity has not however been established. Furthermore, given a choice between carbonyls within a molecule, the nucleophilic attack in the cases studied thus far is on that carbonyl with the greater force constant, that is, the more positive carbon.[46] The electronic effect is dominant over steric requirements in all reported cases where reaction occurs, with one questionable exception.[47] Fischer has indicated work underway in his laboratory testing the magnitude of this electronic *vs.* steric control of attacking nucleophiles.[37]

In conclusion we feel there exists a strong relationship between the calculated force constants as derived from spectroscopic data and chemical reactivity patterns. The data in Table I indicate that small differences in k_1 and k_2 within a given molecule are meaningful.

This initial exposition suggests additional work, including correlation of reaction rates and stereochem-

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(46) The products formed in all cases are believed to be the kinetically controlled product, since under the conditions which these reactions are carried out substituted metal carbonyls have shown no tendency for isomerization.

(47) E. O. Fischer reports that reaction of C_6H_5Li with $Mn_2(CO)_{10}$ results in sterically controlled axial attack whereas CH_3Li attack results in equatorial addition.[40] Simultaneous experiments in our laboratory yielded products which gave identical infrared frequencies in the CO stretching region as those reported by Fischer. However, due to the complexity of these spectra we found it very difficult to assign the stereochemistry of these species based on infrared results only. Needless to say group theoretical considerations in this complex system are of limited value as compared with the mononuclear metal carbonyl species.

istries with force constants, the separation of steric and electronic effects, and the specific role of the organolithium compounds in nucleophilic addition reactions.[48] It is also important to test the hypothesis with nucleophiles derived from reagents other than organolithium compounds.

We have begun an investigation of the reactions of organomagnesium halides with tungsten and chromium hexacarbonyls. Our initial results indicate these reactions provide products identical with those resulting from organolithium–metal carbonyl reactions but seem to be more amenable to a kinetic study.[49]

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[48] Several of these investigations are presently underway in our laboratory.

[49] Reactions of methyl- and phenylmagnesium bromides with tungsten and chromium hexacarbonyls and subsequent ethylation produced complexes identical with those well characterized in the phenyl- and methyllithium reactions.[1] Benzyl- and cyclohexylmagnesium chlorides produced carbene-type ligands hitherto unreported. Further studies of these reactions are forthcoming from our laboratories.

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Mössbauer Spectra of Some Linear and Triangular Polynuclear Iron Carbonyls

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The Mössbauer spectra of ^{57}Fe in a number of trinuclear carbonyls were studied at liquid nitrogen temperature. In the linear $Mn_2Fe(CO)_{14}$ the quadrupole splitting is only 0.43 mm/sec, whereas in the triangular species $(C_2H_5)_4N[Fe_2M(CO)_{12}]$ (M = Mn, Tc, Re) it is much greater (Δ = 0.91, 0.91, and 0.89 mm/sec, respectively). An estimate of 0.15 mm/sec is given for the quadrupole splitting of the unique iron atom in $Fe_3(CO)_{12}$. The isomer shifts are very similar for all of the compounds studied: δ 0.34–0.35 mm/sec relative to sodium nitroprusside. Charge distributions were estimated by analysis of these data. In the linear compound, the small quadrupole splitting was taken as evidence of the rather high σ donation of terminal carbonyls, which also explained the very small quadrupole splitting observed for the unique iron atom in $Fe_3(CO)_{12}$. In the triangular species the environment of the iron atoms may be described as an octahedron with distortions along both the three- and fourfold axes. In comparison with the quadrupole coupling in $Co_2(CO)_8$, it is shown that the observed quadrupole splitting is approximately equal to the contribution of the tetragonal distortion. This part of the field gradient is attributed to the higher metal orbital population in the metal–metal bonds compared with metal–carbon bonds of bridging carbonyls. A value of 0.11 was obtained for the difference in σ donation from terminal and bridging carbonyls to the iron atom.

Introduction

The iron carbonyls were among the first compounds to be studied by the Mössbauer method soon after it was recognized as a source of molecular structure information. Although the structure of triiron dodecacarbonyl, $Fe_3(CO)_{12}$, had not yet been determined satisfactorily, its Mössbauer spectrum[3] showed that two different kinds of iron atoms are present in the molecule. A number of structures were consistent with the data, and as Wertheim[4] pointed out, the structure could not be proved from the Mössbauer spectrum alone. Later, as a consequence of a Mössbauer study of $Fe_3(CO)_{11}H$ by Erickson and Fairhall[5] and an X-ray study by Dahl and Blount[6], the probable structure of $Fe_3(CO)_{12}$ emerged as a triangular array of iron atoms corresponding to the structure of diiron enneacarbonyl in which one of the bridging carbonyls was replaced by a *cis*-octahedral $Fe(CO)_4$ group; this structure has recently been confirmed by Wei and Dahl.[7] Following the work of Erickson and Fairhall, it has been assumed that the outer lines of the $Fe_3(CO)_{12}$ spectrum arise from the carbonyl-bridged $Fe_2(CO)_8$ moiety, and the central line is due to the essentially octahedral $Fe(CO)_4$ group. This assignment has not been fully demonstrated, nor has there been an adequate explanation of the increase in the quadrupole splitting over that observed in the parent $Fe_2(CO)_9$.

During the past decade, a number of mixed-metal carbonyls with metal–metal bonds have been prepared. Among these is a series of triangular group VIIb diiron dodecacarbonyl anions whose proposed structures are like that of $Fe_3(CO)_{12}$ in which the unique iron atom is replaced by a group VIIb atom. Examination of the Mössbauer spectra of this series afforded an opportunity

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