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Activation of the M–CO Bond in Transition Metal Complexes. CO Substitution Reactions in Di-, Tri- and Tetra-nuclear Metal Carbonyl Compounds Catalyzed by $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$

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Abstract

The catalytic activity of $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]_2$ (hereafter $[FeCp]_2$) in the CO substitution reactions has been explored in a number of systems involving binary and organometallic carbonyl complexes of two, three and four nuclearity. The results point out the versatility of $[FeCp_2]$ in promoting CO substitution with various Lewis bases where improved selectivity and yields of the substituted products have been achieved. The $[FeCp]_2$ catalyzed reaction between $[Fe_3(CO)_8(PhC_2Ph)_2]$ (black isomer) and $P(OMe)_3$ afforded, at room temperature, two isomeric monosubstituted products, whose solution structures and dynamics have been elucidated by NMR spectroscopy. It is noteworthy that no substitution products could be obtained in the absence of the catalyst even at elevated temperatures.

Introduction

Recently, the need to avoid drastic and prolonged heating has prompted an active search for reagents able to promote CO substitution reactions on metal carbonyls under mild experimental conditions [1]. In addition, the use of such promoting agents often offers an improved selectivity in the substitution path and sometimes allows the synthesis of novel products not available through the usual thermal routes. The use of Me_3NO (whose attack to a coordinated CO group causes loss of CO_2 and consequent creation of a vacant site) is now a well established procedure in transition metal carbonyl chemistry [2]. Another useful reagent is sodium benzophenone ketyl (BPK). It produces via an electron transfer, radical anions which undergo easy CO substitutions with a variety of nucleophiles [3]. Among the dinuclear complexes, Coville and co-workers have shown that $[FeCp]_2$ acts as a versatile catalyst in promoting ligands substitution (CO, CNR, I) in several (generally mononuclear) systems [4]. We are reporting here the results obtained in a number of CO substitution reactions involving di-, tri- and tetra-nuclear complexes using $[FeCp]_2$ as catalyst.

The extensive study of the reactions catalyzed by this and other dinuclear complexes could provide a better understanding of the chemistry of the carbonyl complexes.

Results and Discussion

The results of the CO substitution reactions are summarized in Table I. Whenever possible these results are compared to those obtained in BPK-promoted reactions and/or in normal thermal routes. When using $[FeCp]_2$ as the catalyst, the substitution occurs in the same sites as found for BPK or thermal routes.

In the case of $Fe_3(CO)_{12}$ as substrate, BPK and thermal routes give poor yields of mono-substituted products. Furthermore, the thermal path provides low yields of bi- and tri-substituted products, while BPK causes extensive cluster fragmentation when further substitutions are attempted. In contrast, the use of $[FeCp]_2$ as the catalyst affords high yields of these three products; their relative amounts depend only on the cluster/ligand ratio employed ($Fe_3(CO)_{12}$/catalyst = 10:1 in all cases).

For the more robust trinuclear cluster $Ru_3(CO)_{12}$, significantly better yields of mono- and bi-substituted products can be obtained using BPK in place of $[FeCp]_2$. However, improved amounts of $Ru_3(CO)_9L_3$ (L = Lewis base) are achieved with $[FeCp]_2$. The use of $[FeCp]_2$ allows more clean substitution reactions in $H_4Ru_4(CO)_{12}$ when compared with other synthetic methods (Table I).

For the organometallic complex $Co_2(CO)_6(PhC_2Ph)$, good to excellent yields of mono-substituted products are obtained simply by a thermal route. Using $[FeCp]_2$ similar yields are achieved more rapidly at the same temperature and reasonable yields are still obtained at lower temperature. The reaction involving $[Fe_3(CO)_8(PhC_2Ph)_2]$ as starting material gives two novel isomeric complexes (Table

TABLE I. Experimental Data for the Reactions between Metal Carbonyl Complexes and Lewis Bases in the Presence of $[FeCp]_2$ as Catalyst[a]

Cluster	Ligand	Molar ratio	Product	$[FeCp]_2$			B.P.K.			Thermal route		
				Time (h)	Temperature (°C)	% Yield	Time (min)	Temperature (°C)	% Yield	Time (h)	Temperature (°C)	% Yield
$Fe_3(CO)_{12}$	PPh_3	1:1	$[Fe_3(CO)_{11}(PPh_3)]$	1.5	40	60	5–15	25–40	26 [3a]	0.75	45	2 [13c]
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:1	$[Fe_3(CO)_{11}(P(OEt)_3)]$	15	25	60				3–6	50	17 [13c]
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:2	$[Fe_3(CO)_{10}(P(OEt)_3)_2]$	15	25	70				3–6	50	25 [13c]
$Fe_3(CO)_{12}$	$P(OEt)_3$	1:3	$[Fe_3(CO)_9(P(OEt)_3)_3]$	3.5	40	40				3–6	50	12 [13c]
$Fe_3(CO)_{12}$	$P(OMe)_3$	1:3	$[Fe_3(CO)_9(P(OMe)_3)_3]$	3.5	40	40				3–6	50	9 [13c]
$Fe_3(CO)_{12}$	$CNBu^n$	1:1	$[Fe_3(CO)_{11}(CNBu^n)]$	1.5	30	75						
$Fe_3(CO)_{12}$	$CNBu^n$	1:2	$[Fe_3(CO)_{10}(CNBu^n)_2]$	2	36	70			n.r. [13a]			
$Ru_3(CO)_{12}$	PPh_3	1:1	$[Ru_3(CO)_{11}(PPh_3)]$	8	25	40	5–15	25–40	81 [3a]	1–3	67	16 [13d]
$Ru_3(CO)_{12}$	PPh_3	1:2	$[Ru_3(CO)_{10}(PPh_3)_2]$	8	25	60	5–15	25–40	96 [3a]			
$Ru_3(CO)_{12}$	PPh_3	1:4	$[Ru_3(CO)_9(PPh_3)_3]$	1	50	80	5–15	25–40	65 [3a]	1–3	67	86 [13d]
$Ru_3(CO)_{12}$	$P(OMe)_3$	1:1	$[Ru_3(CO)_{11}(P(OMe)_3)]$	4	25	60	5–15	25–40	72 [3a]			
$Ru_3(CO)_{12}$	$P(OMe)_3$	1:2	$[Ru_3(CO)_{10}(P(OMe)_3)_2]$	4	25	70						
$Ru_3(CO)_{12}$	$P(OMe)_3$	1:4	$[Ru_3(CO)_9(P(OMe)_3)_3]$	3	45	85				1–3	67	7 [13d]
$Ru_3(CO)_{12}$	dppe	1:1	$[Ru_3(CO)_{10}(dppe)]$	1	45	70	10	40	52 [3b]	1–3	67	3 [13e]
$Ru_3(CO)_{12}$	dppp	1:1	$[Ru_3(CO)_{10}(dppp)]$	1	45	70						
$H_4Ru_4(CO)_{12}$	PPh_3	1:1	$[H_4Ru_4(CO)_{11}(PPh_3)]$	2	36	80	5–15	25–40	55 [3a]	8	100	8.5 [13c]
$H_4Ru_4(CO)_{12}$	PPh_3	1:2	$[H_4Ru_4(CO)_{10}(PPh_3)_2]$	2	40	85				10	66	35 [13c]
$H_4Ru_4(CO)_{12}$	$P(OMe)_3$	1:3	$[H_4Ru_4(CO)_9(P(OMe)_3)_3]$	2	50	90	5–15	25–40	47 [3a]	10	66	40 [13f]
$H_4Ru_4(CO)_{12}$	$P(OMe)_3$	1:5	$[H_4Ru_4(CO)_8(P(OMe)_3)_4]$	2.5	50	75				1	97	61 [13f]
$Co_2(CO)_6(PhC_2Ph)$	PPh_3	1:1	$[Co_2(CO)_5(PPh_3)(PhC_2Ph)]$	5	36	60	5	25	1 [13b]	3	70	84 [13g]
$Co_2(CO)_6(PhC_2Ph)$	PPh_3	1:1	$[Co_2(CO)_5(PPh_3)(PhC_2Ph)]$	1	67	80						
$Fe_3(CO)_8(PhC_2Ph)$	$P(OMe)_3$	1:3	$[Fe_3(CO)_7P(OMe)_3(PhC_2Ph)_2]$	1.5	25	30			10	99	n.r.	
$Fe_3(CO)_8(PhC_2Ph)$	$P(OMe)_3$	1:3	$[Fe_3(CO)_7P(OMe)_3(PhC_2Ph)_2]$	1.5	25	60			10	99	n.r.	

[a] dppe = $Ph_2PCH_2CH_2PPh_2$; dppp = $Ph_2PCH_2CH_2CH_2PPh_2$; n.r. = no reaction.

TABLE II. Spectroscopic Data of the Novel [$Fe_3(CO)_7P(OMe)_3(PhC_2Ph)_2$] Isomers[a]

	Isomer a	Isomer b
IR, ν(CO) (cm^{-1}) (cyclohexane)	2028m, 1998vs, 1989m, 1958s, 1842m, 1820m	2040vs, 2006vs, 1983s, 1971s, 1961s, 1848s, 1837m
^{1}H NMR, δ (ppm) ($CDCl_3$)	7.45–6.41(m, 20); 3.59(d, 9)[b]	7.54–6.61(m, 20); 3.43(d, 9)[b]
^{31}P NMR, δ(ppm)[c] ($CDCl_3$)	147.6	158.0
^{13}C NMR, δ (ppm) ($CDCl_3$) cyclopentadienyl-region	119.4(d, J_{C-P} = 3.3 Hz, $\underline{C1}$); 119.2(s, $\underline{C4}$); 118.4(s, $\underline{C2}$ and $\underline{C3}$)	120.1(s, $\underline{C1}$ and $\underline{C4}$); 117.4(s, $\underline{C2}$ and $\underline{C3}$)
^{13}C NMR, δ (ppm) ($CDCl_3$) carbonyl-region	263.2(d, 2: J_{C-P} = 16.1 Hz) 207.7(d, 1; J_{C-P} = 38.1 Hz) 207.0(s, 2), 200.5(s, 2)	262.1(s, 1)[d]; 255.9(d, 1); 209.8(d, 1); 207.9(s, 1); 206.4(s, 1); 205.5(s, 2)

[a]Both isomers gave satisfactory chemical microanalyses. [b]J_{H-P} = 11.0 Hz. [c]Chemical shifts are reported downfield positive to external H_3PO_4 85%. [d]Limiting spectrum at –60 °C.

II), whose solution structures will be discussed in detail below.

The most important generalizations from the bulk of the experimental data are:

(a) the substitution rates are roughly proportional to the amount of $[FeCp]_2$;

(b) the substitution rates increase as the temperature is raised;

(c) no significant difference is observed between reactions brought about in daylight or in the dark;

(d) only a partial recovery of the catalyst is obtained at the end of the substitution reactions; the decomposition of the catalyst increases with temperature and/or reaction time;

(e) the reaction rates are noticeably quenched by addition of the radical inhibitor galvinoxyl.

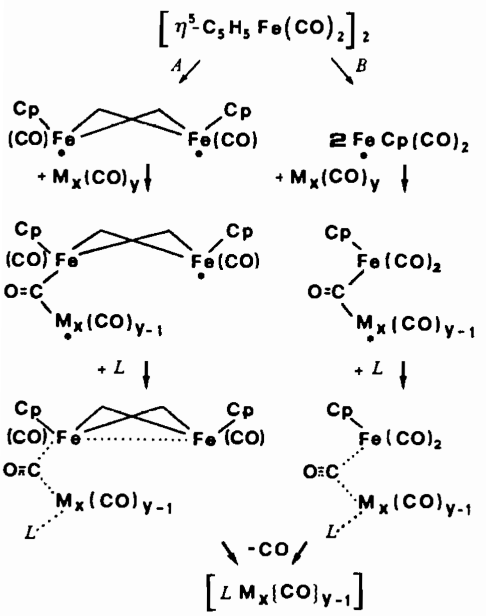
In order to get more insight into the catalytic mechanism carried out by $[FeCp]_2$, an n-hexane solution of this complex is stirred in presence of the spin-trap α-phenyl-t-buthyl-nitrone (PBN) [5] at +40 °C. After few minutes a strong ESR signal is detected; its intensity increases with reaction time and/or temperature (up to +60 °C). Interestingly, under the same experimental conditions mononuclear complexes such as $Fe(CO)_5$ and $Cr(CO)_6$ as well as the binuclear compounds $Co_2(CO)_8$ and $[Ni(\eta^5\text{-}C_5H_5)CO]_2$ do not afford any radical species which can be trapped by PBN. On the other hand, several derivatives such as $[Co_2(CO)_6(PPh_3)_2]$, $[Mn_2(CO)_9(PPh_3)]$, $[Mn_2(CO)_8(PPh_3)_2]$ and $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]_2$ prove to be ESR-active and at the same time show detectable catalytic activity in the substitution reactions. They are, however, poorer catalysts than $[FeCp]_2$.

The appearance of spin-trapped radicals deriving from dimetallic complexes has already been reported by Lappert and co-workers [6] using photochemical activation at low temperature. The use of 2,3,5,6-tetramethyl-1-nitrosobenzene (RNO) as the spin-trap allowed them to observe hyperfine couplings with magnetically active metallic centers, thus confirming that the radicals were actually formed by cleavage of a metal–metal bond. Unfortunately, the RNO cannot be used at temperatures above +20 °C and, since our experiments are carried out at higher temperatures, we are not able to establish the actual nature of the radical species.

On the basis of the bulk of these observations, Scheme 1 is proposed. Path *A* should be more important at low temperature (since intramolecular radical recombination is generally very fast, it is not expected to be very active in the overall substitution reactions). On the other hand, path *B* – responsible for the decomposition of the catalyst – should predominate at high temperature.

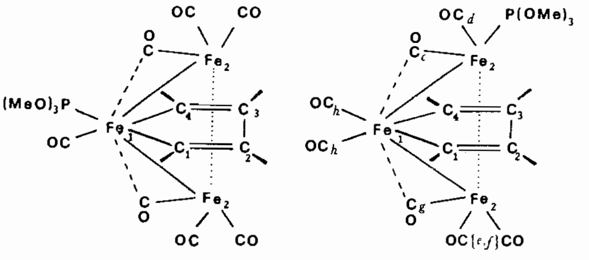
$P(OMe)_3$ Substituted Derivatives of [$Fe_3(CO)_8$-($PhC_2Ph)_2$]

The use of $[FeCp]_2$ proves to be particularly important in the case of $P(OMe)_3$ substitution of $[Fe_3(CO)_8(PhC_2Ph)_2]$ (black isomer), where the direct thermal route does not afford any product, even in n-heptane after reflux for several hours. In the presence of $[FeCp]_2$ the same reaction gives rise to two isomeric mono-substituted products of the formula $[Fe_3(CO)_7P(OMe)_3(PhC_2Ph)_2]$, which can be easily separated by TLC workup. These two complexes are fully characterized by IR and multinuclear NMR spectroscopy. In particular, ^{1}H and ^{13}C NMR spectra of the organic moiety of both isomers



Scheme 1.

indicate that the metalla-cyclopentadienyl system is retained. Thus, the two isomers should differ only in the phosphite substitution site (Table II).



isomer **a** isomer **b**

Fig. 1. Proposed structures of the two $[Fe_3(CO)_7P(OMe)_3(PhC_2Ph)_2]$ isomers (phenyl groups omitted for clarity). In isomer **b**, each carbonyl group is labelled according to the assignment of its ^{13}C NMR spectrum.

In the carbonyl region isomer **a** shows, at room temperature, four absorptions in the relative intensity ratio of 2:1:2:2. The presence of two equivalent bridging COs is inferred from the low field chemical shift of the resonance of intensity 2 at 263.2 ppm, which appears as a doublet due to the phosphorous coupling. Thus in isomer **a** the substitution has occurred on the central iron atom Fe_1 (Fig. 1).

The ^{13}C carbonyl region of isomer **b**, at −60 °C, shows six resonances in the relative intensity ratio of 1:1:1:1:1:2 (Fig. 2); the two lower field absorptions are assigned to non-equivalent bridging COs. Interestingly, only the resonances at 255.9 (CO_c) and 209.8 (CO_d) ppm showed couplings with ^{31}P of 23.4 and 60.1 Hz respectively. As the temperature is increased these two resonances broaden and disappear into the base line ($\Delta G^* = 11.1 \pm 0.5$ kcal/mol); the equilibration of these carbonyls corresponds to a localized CO exchange at the substituted Fe_2 center. This process can also be observed from the averaging of the J_{C-P} couplings in the V.T. ^{31}P spectra of a ^{13}CO-enriched sample of isomer **b** (Fig. 3).

At +25 °C the two absorptions of relative intensity 1 at 207.9 and 206.4 ppm (Co_e and Co_f) have coalesced to a broad peak (as a result of the averaging process occurring on $Fe(CO)_2P(OMe)_3$ moiety) and at higher temperature (+60 °C) they are involved in a fast exchange process with the bridging CO_g at 262.1 ppm. The resonance of intensity 2 (205.5 ppm CO_h) remains very sharp up to +80 °C. The overall dynamic behaviour of isomer **b** parallels that found for the unsubstituted compound [7], but the phosphite stabilizes the carbonyl bridged ground state, raising the $\Delta G^{\ddagger}$ for the localized bridge-terminal CO exchange.

There are some interesting differences between the two isomers arising from the different position of the ligand:

(a) a downfield shift (+7.3 ppm) is observed on passing from isomer **b** to isomer **a** for the CO group bridging Fe_1 and Fe_2;

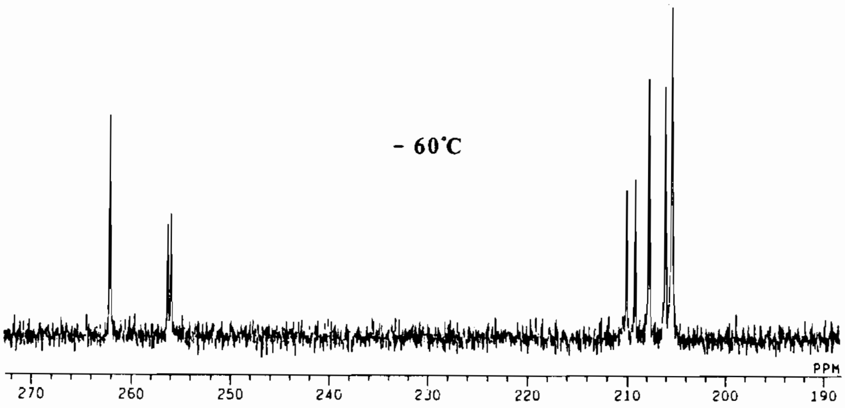


Fig. 2. ^{13}C NMR low-temperature limiting spectrum ($CDCl_3$) of isomer **b** in the carbonyl region.

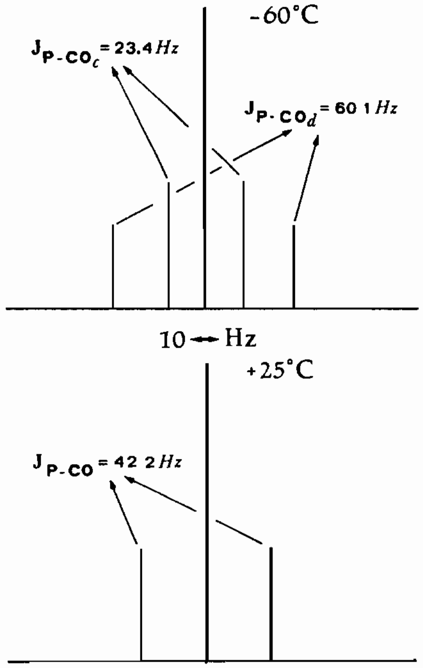


Fig. 3. Sketch of the V.T. ^{31}P NMR spectra (CDCl$_3$) of a ^{13}CO-enriched sample of isomer **b**.

(b) the energy barrier for the localized CO$_{\text{bridging}}$/CO$_{\text{terminal}}$ exchange at the Fe$_2$ centers follows the order: Fe$_{(2)}$(CO)$_3$(isomer **a**) > Fe$_{(2)}$(CO)$_3$(isomer **b**) > Fe$_{(2)}$(P(OMe)$_3$)(CO)$_2$(isomer **b**). Both features can be accounted for in terms of a strengthening of the moiety μ_2(Fe$_1$—CO—Fe$_2$) on the side at which the P(OMe)$_3$ substitution takes place

Experimental

The complex [Fe(CO)$_2$(η^5-C$_5$H$_5$)]$_2$ was purchased from Strem Chemicals, the ligands employed from Fluka A.G. The parent compounds Fe$_3$(CO)$_{12}$ [8], Ru$_3$(CO)$_{12}$ [9], H$_4$Ru$_4$(CO)$_{12}$ [10], Co$_2$(CO)$_6$-(PhC$_2$Ph) [11] and Fe$_3$(CO)$_8$(PhC$_2$Ph) [12] were prepared by published procedures or modifications thereof. All the substitution reactions were routinely brought about in double-necked flasks wrapped in aluminium foil and immersed in a water-bath maintained at the desired temperature. The substrate/catalyst ratio was always 10:1. The reactions were checked by TLC and IR spectroscopy.

Elemental analyses were obtained from Pascher Microanalytisches Laboratory, Bonn, F.R.G. ESR spectra were recorded on a Varian E 109 Spectrometer in the X band mode, ^{1}H, ^{13}C and ^{31}P NMR spectra on a Jeol GX-270/89 spectrometer and IR spectra on a 580 B Perkin-Elmer instrument with a data station.

Preparation of [Fe$_3$(CO)$_7$P(OMe)$_3$(PhC$_2$Ph$_2$)] Isomers

[Fe$_3$(CO)$_8$(PhC$_2$Ph)$_2$] (200 mg, 0.23 mmol), P(OMe)$_3$ (86 mg, 0.70 mmol) and [FeCp]$_2$ (8 mg, 0.02 mmol) were stirred in 150 ml of cyclohexane at room temperature for 1.5 h. The reaction mixture was filtered, concentrated under reduced pressure and separated by TLC (SiO$_2$, eluant petroleum ether and 10% diethyl ether) to give the brown isomer **a** (≅30%) and the dark-green isomer **b** (≅60%), both compounds were recrystallized from n-hexane-CHCl$_3$ (2:1 *v/v*) solutions kept under N$_2$ at −20 °C.

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