Organometallics **1990**, *9*, 929–935

Reactions of Organic Halides with the Carbonyl Anions $[M(CO)_4]^-$ (M = Rh, Ir). Crystal and Molecular Structure of $[PPN][IrBr_2(CO)_2(CH_2CO_2Me)_2]$ and of $[PPN][Ir(CO)_2(CH_2CN)_2]$ ($PPN^+ = [(Ph_3P)_2N]^+$)

Francesca Porta, Fabio Ragaini, and Sergio Cenini*

Dipartimento di Chimica Inorganica e Metallorganica and CNR Center, Via Venezian 21, 20133 Milano, Italy

Francesco Demartin

Istituto di Chimica Strutturistica Inorganica and CNR Center, Via Venezian 21, 20133 Milano, Italy

Received May 23, 1989

By reaction of $[PPN][Ir(CO)_4]$ (**1**, PPN = $[(Ph_3P)_2N^+]$) with $BrCH_2R$ (R = CO_2Me, CN, Ph), the anionic derivatives, *all cis*-$[PPN][IrBr_2(CO)_2(CH_2R)_2]$ [R = CO_2Me (**3a**), CN (**3b**), Ph (**3c**)] have been obtained. The structure of these compounds, suggested by IR and NMR data, has been unambiguously clarified in the case of compound **3a** by X-ray crystallography. Compound **3a** crystallizes in the triclinic space group $P\bar{1}$, with a = 9.882 (2), b = 14.642 (3), c = 16.076 (3) Å, α = 105.59 (2), β = 102.44 (2), γ = 99.52 (2)°, Z = 2. R = 0.036 and R_w = 0.046 for 5595 reflections with $I > 3\sigma(I)$. Analogous reactions carried out on $[PPN][Rh(CO)_4]$ (**2**) allowed only the isolation of *cis*-$[PPN][RhBr_2(CO)_2]$ (**9**). Spectroscopic studies have shown that intermediates in these reactions are the complexes *cis*-$[PPN][MBr(CO)_2(CH_2R)]$ [M = Rh, R = CO_2Me, CN (**4a,b**); M = Ir, R = CO_2Me, CN (**5a,b**)]. By carbonylation of **3c** at atmospheric pressure, the anionic iridium bis-acyl derivative $[PPN][IrBr_2(CO)_2(COCH_2Ph)_2]$ (**6**) has been identified by spectroscopic measurements. The reaction is reversible, and by bubbling dinitrogen into a solution of **6**, compound **3c** is re-formed. On the other hand, the reaction of **1** with $PhCH_2COCl$ gave the monoacyl derivative, $[PPN][IrCl_3(CO)_2(COCH_2Ph)]$ (**7**). By treatment of compound **3b** with sodium methoxide, a complex reaction was observed, from which it was possible to isolate only the complex $[PPN][Ir(CO)_2(CH_2CN)_2]$ (**8**), the structure of which was determined by single-crystal X-ray diffraction. Compound **8** is triclinic, space group $P\bar{1}$, with a = 9.684 (1), b = 13.994 (1), c = 15.055 (1) Å, α = 74.92 (1), β = 85.89 (1), γ = 74.67 (1)°, Z = 2. R = 0.039 and R_w = 0.058 for 3934 reflections with $I > 3\sigma(I)$. Compounds **1** and **2** have been tested as catalysts in the carbonylation of $PhCH_2Br$, showing a low catalytic activity and a poor selectivity in the formation of $PhCH_2COOH$.

Introduction

Studies on the synthesis and reactivity of the alkylcobalt carbonyl derivatives $Co(CO)_4R$ represent an area of current interest. On one hand, these compounds are the intermediates formed during the hydroformylation reaction catalyzed by cobalt carbonyl.[1] On the other hand, these compounds are intermediately formed during the single and double carbonylation of benzyl halides, catalyzed by the tetracarbonylcobaltate anion in the presence of sodium or calcium hydroxides.[2] In the latter case, the carbonylation of alkyl halides bearing electron-withdrawing groups requires, when conducted in mild conditions, the presence of sodium methoxide.[2] We have investigated the reactions of the carbonyl anions $[M(CO)_4]^-$ (M = Rh, Ir) with alkyl halides, even substituted with electron-withdrawing groups, in order to study the effect of the nature of the metal in these reactions. The reactions of the iridium compounds have been summarized in Scheme I. To the best of our knowledge, only one paper marginally related to our work, dealing with the reaction of the iridium anion $[Ir(CO)_3PPh_3]^-$ with methyl iodide, has been reported.[3] However, this latter reaction gives a product of a nature different from those observed by us.

Results and Discussion

Reactions of the $[M(CO)_4]^-$ Anions (M = Rh, Ir) with Organic Halides. By reaction of $[PPN][Ir(CO)_4]$ (**1**, PPN = $[(Ph_3P)_2N]^+$) with $BrCH_2R$ (R = CO_2Me, CN, Ph) in THF and under a dinitrogen atmosphere, we have isolated the products of the double oxidative addition of the organic bromides to the iridium center (eq 1). Even

$$\underset{\mathbf{1}}{[PPN][Ir(CO)_4]} + 2BrCH_2R \xrightarrow{THF} cis\text{-}[PPN][IrBr_2(CO)_2(CH_2R)_2] + 2CO \quad (1)$$
$$R = CO_2Me\ (\mathbf{3a}),\ CN\ (\mathbf{3b}),\ Ph\ (\mathbf{3c})$$

by conducting this reaction with a 1:1 ratio of the reactants (R = CO_2Me, CN), the final products are mainly compounds **3a** or **3b**, in the presence of unreacted $[PPN][Ir(CO)_4]$ (**1**) and of the products of the monooxidative addition (see later). Compounds **3a–c** show in their IR spectra two γ_{CO} of equal intensity in the 2000–2100-cm^{-1} region (Table I), suggesting a cis coordination of the two carbonyl ligands. The bidimensional NMR spectra, $^1H_{corr}$ COSY 90, of these compounds have shown two nonequivalent $-CH_2-$ groups, with a geminal coupling of the two hydrogens (Table I). The two protons of each $-CH_2-$ group are nonequivalent in the NMR spectrum since complexes **3a–c** are chiral, existing as a mixture of two enantiomers of configuration Δ and Λ.

For compound **3a** the $^{13}C-^1H_{corr}$ NMR spectrum was also recorded. For these and other complexes described below, very low values for the IR stretching frequencies of the ester and cyano groups and an extremely low field ^{13}C NMR signal for the carbon atom of the $-CO_2-$ group were always found (Table I). The assignment of the signal at 181.3 ppm, in the ^{13}C NMR spectrum of **3a**, to the carbon atom of the ester group has been confirmed by detection of the long-range C–H coupling constant (J_{C-H} = 4.2 Hz) with the methylene group.

---

[1] Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P. Eds.; Wiley: New York, 1977; Vol. II.

[2] Foà, M.; Francalanci, F. *J. Mol. Catal.* **1987**, *41*, 89.

[3] Collman, J. P.; Vastine, F. D.; Roper, W. R. *J. Am. Chem. Soc.* **1968**, *90*, 2282.

0276-7333/90/2309-0929$02.50/0

Scheme I

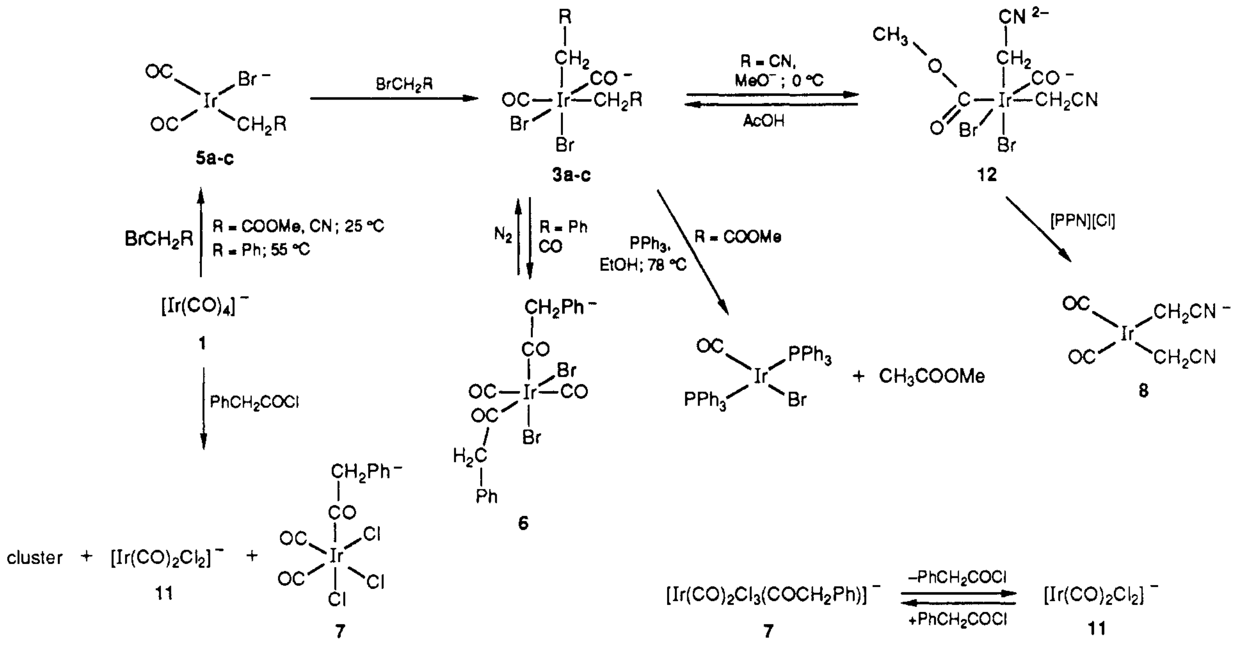


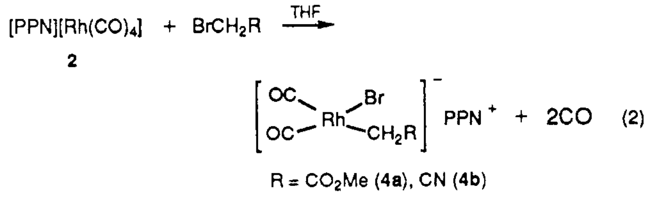
Table I. IR[a] and ¹H and ¹³C NMR[b] Data[e]

compound	ν_{CO}	$\nu_{C=O \text{ or } CN}$	δ_{CH_2} (¹H)	δ_C (¹³C)
[PPN][$IrBr_2(CO)_2(CH_2CO_2Me)_2$] (**3a**)	2095–2037	1712	H_A = 2.7 (d), H_B = 3.15 (d), $J_{A\text{-}B}$ = 9 H_C = 2.73 (d), H_D = 3.34 (d), $J_{C\text{-}D}$ = 8.8	CH_2 = 16.1–4.5, OCH_3 = 50.8–50.1 CO = 164.9–158.1, CO_2CH_3 = 181.3
[PPN][$IrBr_2(CO)_2(CH_2CN)_2$] (**3b**)	2105–2047	2213	H_A = 2.75 (d), H_B = 2.28 (d), $J_{A\text{-}B}$ = 15.1 H_C = 2.57 (d), H_D = 2.23 (d)), $J_{C\text{-}D}$ = 14.6	
[PPN][$IrBr_2(CO)_2(CH_2Ph)_2$] (**3c**)	2079–2017		H_A = 3.82 (d), H_B = 3.23 (d), $J_{A\text{-}B}$ = 9.5 H_C = 4.16 (d), H_D = 3.23 (d), $J_{C\text{-}D}$ = 9.6	
[PPN][$RhBr(CO)_2(CH_2CO_2Me)$] (**4a**)	2035–1957	1695	2.73 (d), $J_{Rh\text{-}H}$ = 2.68[c]	
[PPN][$RhBr(CO)_2(CH_2CN)$] (**4b**)	2041–1961	2193		
[PPN][$IrBr(CO)_2(CH_2CO_2Me)$] (**5a**)	2025–1935	1700	2.18[d]	
[PPN][$IrBr(CO)_2(CH_2CN)$] (**5b**)	2031–1949	2201	1.55[d]	
[PPN][$IrBr_2(CO)_2(COCH_2Ph)_2$] (**6**)	2058	1665–1646	4.21[d]	CH_2 = 66.9, CO = 167.8 $COCH_2$ = 201.1
[PPN][$IrCl_3(CO)_2(COCH_2Ph)$] (**7**)	2119–2063	1676	4.53	CH_2 = 60.9, CO = 152.9 $COCH_2$ = 196.9
[PPN][$Ir(CO)_2(CH_2CN)_2$] (**8**)	2015–1940	2195	1.37[d]	

[a] cm^{-1}, in THF. [b] δ/ppm, J values in hertz; in $CDCl_3$. [c] In chlorobenzene. [d] In CD_3COCD_3. [e] Other relevant ¹H NMR signals: **3a**, δ 3.62, 3.61 (s, CH_3); **4a**, δ 3.64 (s, CH_3); **5a**, δ 3.44 (s, CH_3). For compounds **3c**, **6**, and **7** the resonances of the aromatic protons have been observed at around δ 7.1–7.2. In the ¹³C NMR spectra of compounds **6** and **7**, the signals of aromatic carbon atoms fall together with the more intense signals of the PPN countercation in the 125–137 ppm region and are not easily identified.

The observed shifts in the IR spectra are typical of unsaturated groups bearing in β a transition metal. This has been called the "β effect" and explained as an electron donation from the d orbitals of the metal to the unsaturated group.[4] This effect was also detected for complexes of general formula $RO_2CCH_2Co(CO)_3L$ (L = CO, EPh_3; E = P, As, Sb) and has been tentatively ascribed to an electron donation from the ester group to a coordinated CO.[5] However the very high pK_a of the related compound η^5-$C_5H_5Fe(CO)_2CH_2COOH$[6] seems to imply that the originally proposed explanation is the correct one. The all-cis structure of these compounds has been unambiguously clarified in the case of **3a** by X-ray crystallography (see later; Figure 1).

When reaction 1 was conducted on [PPN][$Rh(CO)_4$] (**2**) with a stoichiometric quantity of organic bromides (R = CO_2Me, CN), it was possible to observe the formation in solution only of the complexes reported in eq 2.



Contrary to iridium, the use of an excess of organic bromides led only to the formation of [PPN][$RhBr_2(CO)_2$] (**9**).[7] When a very large excess (>10:1 mole to mole) of organic bromide was used, the main product was [PPN]$_2$[$RhBr_5(CO)$] (**10**).[8] Both products were identified by

---

(4) (a) Green, M. L. H. In *Organometallic Compounds*; Coates, G. E., Green, M. L. H., Wade, K., Eds.; Methuen: New York, 1968; Vol. II. (b) Flood, T. C.; Di Santi, F. J.; Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

(5) Galamb, V.; Palyi, G.; Cser, F.; Furmanova, M. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1981**, *209*, 183.

(6) Green, M. L. H.; Ariyaratne, J. K. P.; Bierrum, A. M.; Ishaq, M.; Prout, C. K. *Chem. Commun.* **1967**, 430.

(7) Vallarino, L. M. *Inorg. Chem.* **1965**, *4*, 161.

(8) Forster, D. *Inorg. Chem.* **1969**, *8*, 2556.

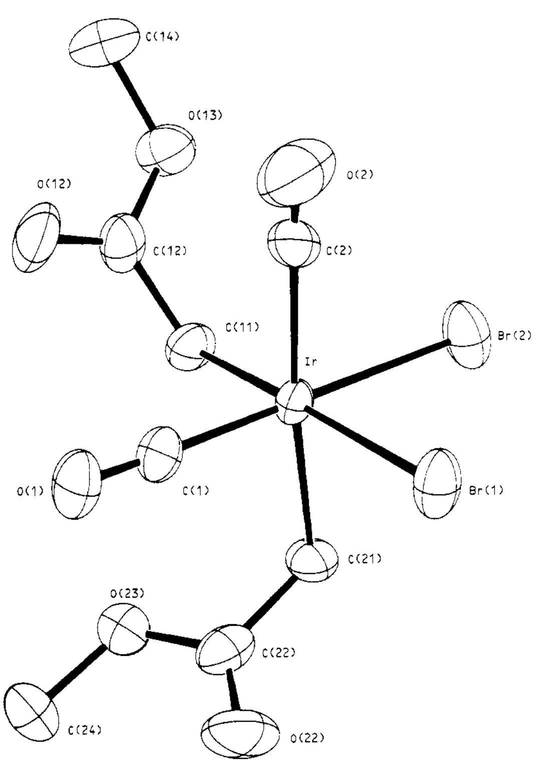


Figure 1. ORTEP drawing of the $[IrBr_2(CO)_2(CH_2CO_2Me)_2]^-$ anion. Thermal ellipsoids are drawn at 30% probability.

comparison of their IR spectra with those of authentic samples prepared by methods reported in literature.[7,8] The formation of $[RhBr_5(CO)]^{2-}$ is not too surprising since the analogous formation of $[RhI_5(CO)]^{2-}$ after a long reaction time between $[RhI_2(CO)_2]^-$ and CH_3I or CH_3CH_2I has been reported.[8] After the transformation into compounds **9** and **10**, the organic ligand is present in solution as the hydrogenated product CH_3R. No traces of other compounds such as RCH_2CH_2R were detected by gas chromatographic analysis.

If a substoichiometric quantity of organic bromide is used in reaction 2, a further transformation takes place, at a much slower rate, involving **4** and the remaining $Rh(CO)_4^-$, leading without observable intermediates, to the formation of a cluster compound. The clusters (from **4a** and **4b**) can be almost quantitatively obtained by using a 3:5 molar ratio bromide/$Rh(CO)_4^-$. Their crystal structure determination is under way, and these compounds will be described in a forthcoming paper.

Attempts at effecting reaction 2 with benzyl bromide failed, because this last compound is less reactive then the other two. Moreover it probably gives a complex less stable, and thus only $[RhBr_2(CO)_2]^-$ is detectable in this case.

Complexes of the type *cis*-$[PPN][IrBr(CO)_2(CH_2R)]$ [R = CO_2Me (**5a**), CN (**5b**)], corresponding to the rhodium compounds **4**, could be also detected by IR when conducting reaction 1. In the case of iridium, however, the second oxidative addition is quicker than the first and compounds **5** never accumulate to a large extent in solution. All the compounds of type **4** and **5** are not stable and could not be isolated. However the spectroscopic data reported in Table I clearly support the proposed structure. Compound **4a** shows two γ_{CO} of equal intensity at 2035 and 1957 cm^{-1}, typical of a *cis*-dicarbonyl structure and a band at 1695 cm^{-1} due to γ_{C-O} of the carbomethoxy group. The total integrated absorption of the 2035-cm^{-1} band is somewhat higher (1:0.9) than that of the 1957-cm^{-1} one. This fact excludes the possibility that the two absorptions are due to three CO groups in any arrangement. Compounds **4** and **5** have the metal in the +1 oxidation state, and, in fact, the IR absorptions of the iridium derivatives are at lower frequencies with respect to those of compounds **3a** and **3b**, which have the metal in the +3 oxidation state. The IR absorption frequencies of compounds **4** are even lower than those of compound **9**, in agreement with the replacement of one bromine ligand by a less electron-withdrawing group such as $-CH_2R$. Reaction 2 was also conducted in chlorobenzene, in order to record directly the ^1H NMR spectrum of the product. The ^1H NMR spectrum of **4a** showed a singlet at δ 3.64, due to the $-CO_2Me$ group, and a doublet at δ 2.73 (J = 2.68 Hz), attributable to the $-CH_2-$ group directly bound and coupled with rhodium. Moreover, during the reactions there was no formation of PPNBr, which is only slightly soluble in THF, and this confirms that bromine is coordinated to the metal (indeed, when the reaction is directed toward the synthesis of the cluster compounds, during the second part of the reaction, in which bromide ion is delivered, an abundant precipitate of PPNBr is observed).

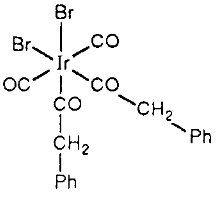
Reaction 1 was also conducted in $(CD_3)_2CO$, with the ^1H NMR spectrum being recorded at different times. Signals at δ 2.18 (CH_2) and 3.44 (CH_3) in the case of $BrCH_2COOMe$ and δ 1.55 (CH_2) in the case of $BrCH_2CN$ were seen to rise and then disappear with concomitant rising of the signals of the final products **3a** and **3b**. The position of the CH_2 signals in compounds **5** are quite upfield with respect to those of the corresponding Ir(III) complexes. On the other hand they are close to the value of δ 1.37 observed in the same solvent for $[PPN][Ir(CO)_2(CH_2CN)_2]$, the structure of which has been determined by crystallographic methods (see later). Even in this case no precipitation of PPNBr was observed. The identity of the countercation in these reactions is very important. When $Na[Ir(CO)_4]$ was used in place of $[PPN][Ir(CO)_4]$, under the same conditions, in the reaction with $BrCH_2COOMe$, two clusters, $[Ir_4(CO)_{10}(CH_2COOMe)_2]^{2-}$ and $[Ir_4(CO)_{11}(CH_2COOMe)]^-$, were obtained instead of **3a**. The structures of their PPN salts have been determined by X-ray crystallographic methods and will be described in a forthcoming paper.

Reactivity of Compounds 3a–c. Compounds **3a** and **3b** do not react in THF with carbon monoxide at atmospheric pressure, as one would expect since the electron-withdrawing groups inhibit the attack to coordinated CO. On the contrary, compound **3c** readily inserts carbon monoxide into the two iridium–carbon bonds (eq 3); see

$$\underset{\textbf{3c}}{[PPN][IrBr_2(CO)_2(CH_2Ph)_2]} + 2CO \underset{N_2}{\overset{THF}{\rightleftarrows}} \underset{\textbf{6}}{[PPN][IrBr_2(CO)_2(COCH_2Ph)_2]} \quad (3)$$

Table I. The reaction is reversible, and by bubbling dinitrogen into a solution of **6**, compound **3c** is obtained again. Compound **6** remained unchanged when it was treated in THF with 50 atm of CO at room temperature and at 50 °C. The complex $[PPN][IrBr_2(CO)_2(COCH_2Ph)_2]$ (**6**) could not be isolated since it reverts to compound **3c** during the workup, and it was characterized only by spectroscopic data in solution. This derivative shows a single γ_{CO} at 2058 cm^{-1}, which indicates a trans configuration of the carbonyl ligands, and two bands at 1665 and 1646 cm^{-1}, attributable to the two acyl groups bound to the metal. Reaction 3 was also conducted in deuterated acetone, in order to record the ^1H and ^{13}C NMR spectra, without isolating the product. In the ^1H NMR spectrum a signal was observed at δ 4.21, attributable to the equivalent $-CH_2-$ groups of the acyl ligands. In the

^{13}C NMR spectrum three singlets have been observed at 66.9, 167.8, and 201.1 ppm, attributable to the $-CH_2-$ groups, to the carbonyl ligands, and to the C=O acyl groups respectively. On these bases the following structure can be suggested:



6

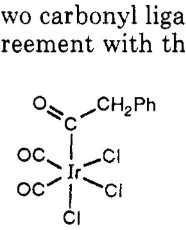
where the two acyl groups are mutually cis, in order to avoid their reciprocal trans influence. The conductivity of a solution of 6 has also been measured. Supposing the proposed formulation, a value of $\Lambda_M = 90.8\ \Omega^{-1}\ cm^{-2}\ mol^{-1}$ in acetone is obtained. This compares very well with the value of $\Lambda_M = 91.1\ \Omega^{-1}\ cm^{-2}\ mol^{-1}$ obtained for $[PPN][IrBr_2(CO)_2(CH_2Ph)_2]$, thus supporting its monomeric nature.

By comparison, we have also carried out the reaction between $[PPN][Ir(CO)_4]$ (1) and $PhCH_2COCl$ (eq 4); see

$$\underset{1}{[PPN][Ir(CO)_4]} + PhCH_2COCl \xrightarrow{THF}$$
$$\underset{11}{[PPN][IrCl_2(CO)_2]} \overset{PhCH_2COCl}{\rightleftharpoons} \underset{7}{[PPN][IrCl_3(CO)_2(COCH_2Ph)]} \quad (4)$$

Table I. In this case the reaction is more complex. By IR spectroscopy it was possible to identify the intermediate formation of $[PPN][IrCl_2(CO)_2]$ (11),[9] which by further reaction with $PhCH_2COCl$ gives compound 7. This was confirmed by reacting an authentic sample of $[PPN][IrCl_2(CO)_2]$ (11) with an excess of $PhCH_2COCl$. An excess of $PhCH_2COCl$ is necessary since 7 is in equilibrium with $[PPN][IrCl_2(CO)_2]$ (11). In fact when pure 7 is dissolved in a solvent such as THF, it slowly equilibrates with the $[IrCl_2(CO)_2]^-$ anion (IR evidence). On the other hand, and contrary to the other acyl complex 6, $[IrCl_3(CO)_2(COCH_2Ph)]^-$ does not show any tendency to decarbonylate to $[IrCl_3(CO)_2(CH_2Ph)]^-$ even when left for prolonged periods in solution under a dinitrogen atmosphere, as evidenced by the absence of any shift in the γ_{CO} frequencies in the IR spectrum.

In reaction 4 other products are formed (IR evidence) that have not been identified. The spectroscopic data for compound 7 (two γ_{CO} of equal intensity and with frequencies typical for an iridium(III) derivative and the equivalence of the two carbonyl ligands in the ^{13}C NMR spectrum) are in agreement with the structure



7

This structure is further supported by the ν_{Ir-Cl} observed at 310, 335, and 345 cm-1.

To verify if a neutral ligand could induce, in more drastic conditions, the insertion of CO into the Ir–C bond and/or the reductive elimination of the organic groups, compound 3a was treated with PPh_3 at reflux in ethanol (eq 5).

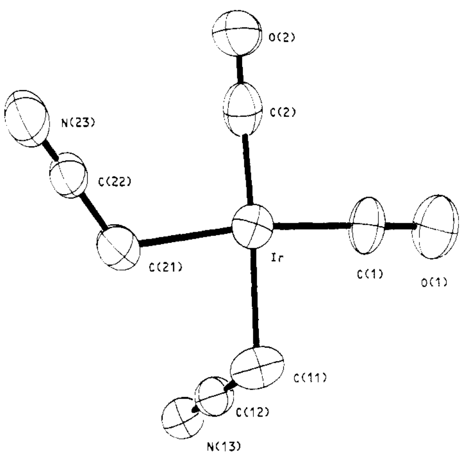


Figure 2. ORTEP drawing of the $[Ir(CO)_2(CH_2CN)_2]^-$ anion. Thermal ellipsoids are drawn at 30% probability.

$$\underset{3a}{[PPN][IrBr_2(CO)_2(CH_2CO_2Me)_2]} \xrightarrow[EtOH\ reflux]{PPh_3}$$
$$IrBr(CO)(PPh_3)_2 + PPNBr + CO + 2CH_3CO_2Me \quad (5)$$

However, while the complex is transformed into $IrBr(CO)(PPh_3)_2$[10] and PPNBr, the organic ligand was recognized by gas chromatographic analysis as methyl acetate, formed by hydrogen abstraction from the solvent.

We finally studied the reactivity of compound 3b with sodium methoxide. A complex reaction was observed in various experimental conditions. In THF, at 0 °C and by adding dropwise a solution of the alcoholate in methanol until the disappearance in the IR spectrum of the absorptions due to compound 3b, a species was observed in solution with IR absorptions at 2210 (w), 2191 (w), 2012 (s), and 1615 (w) cm-1. By addition at this stage of the reaction of acetic acid to the solution, compound 3b is immediately obtained again. This species is probably derived by attack of MeO^- to coordinated carbon monoxide. However when we attempted its isolation by adding PPNCl to the solution, we obtained in low yields only a complex of composition *cis*-$[PPN][Ir(CO)_2(CH_2CN)_2]$ (8, Table I), the structure of which was confirmed by X-ray crystallography (see later and Figure 2).

Catalytic Carbonylations of Benzyl Bromide. Benzyl chloride does not react with the $[M(CO)_4]^-$ (M = Rh, Ir) anions, even by warming the solutions in THF to 60 °C and in the presence of aqueous sodium hydroxide. For this reason we used as substrate the more reactive benzyl bromide. By using $[PPN][Rh(CO)_4]$ (2) as catalyst in THF, with a substrate/catalyst ratio of 10, in the presence of NaOH at atmospheric pressure of carbon monoxide, we observed a complete conversion at 55 °C (Table II, run 2). However the selectivity in the formation of $PhCH_2COOH$ was very poor (2 mol of acid are formed per mol of catalyst). A higher CO pressure (run 3) had practically no effect on the selectivity. No products of the double carbonylation of the benzyl bromide were detected. By gas chromatography–mass spectrometry a variety of organic products was identified, suggesting the intermediate formation of organic radicals in this reaction. By using a higher temperature and a greater amount of NaOH (run 4), the selectivity in the formation of $PhCH_2COOH$ decreases and the primary product becomes $PhCH_2OH$,

---

[9] Forster, D. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 433.

[10] Chatt, J.; Johnson, N. P.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 604.

Table II. Catalytic Carbonylation of $PhCH_2Br$ with $[PPN][Rh(CO)_4]$ (2) as Catalyst[a]

run	T, °C	t, h	P_{CO}, atm	conversion, %	selectivity on $PhCH_2COOH$,[b] %
1	20	48.0	1	95	6
2	55	5.5	1	100	20
3	55	5.5	50	100	22
4	65	3.0	1	100	13[c,d]

[a] Moles of $PhCH_2Br$ = 1.35; substrate/catalyst = 10; NaOH/substrate = 1.4; in THF (10 mL)–water (1 mL). [b] Calculated with respect to converted $PhCH_2Br$. [c] 70% of $PhCH_2OH$ was also formed. [d] THF (4 mL) with 0.5 mL of water saturated with NaOH (40%).

Table III. Crystallographic Data for Compounds 3a and 8

	$[PPN][IrBr_2(CO)_2(CH_2CO_2Me)_2]$	$[PPN][Ir(CO)_2(CH_2CN)_2]$
formula	$C_{44}H_{40}Br_2IrNO_6P_2$	$C_{42}H_{34}IrN_3O_2P_2$
fw	1092.78	866.91
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.882 (2)	9.684 (1)
b, Å	14.642 (3)	13.994 (1)
c, Å	16.076 (3)	15.055 (1)
α, deg	105.59 (2)	74.92 (1)
β, deg	102.44 (2)	85.89 (1)
γ, deg	99.52 (2)	74.67 (1)
V, Å^3	2125 (2)	1899.9 (3)
Z	2	2
D_{calcd}, g cm^{-3}	1.707	1.515
μ(Mo Kα), cm^{-1}	51.11	36.20
min trans factor	0.73	0.74
scan mode	ω	ω
ω scan width, deg	$1.0 + 3.5 \tan\theta$	$1.2 + 0.35 \tan\theta$
θ range, deg	3–25	3–23
octants of reciprocal space explored	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
measd reflns	7452	5670
unique obsd reflns with $I > 3\sigma(I)$	5595	3934
final R and R_w indexes[a]	0.036, 0.046	0.039, 0.058
no. of variables	320	451
esd[b]	1.754	2.080

[a] $R = [\sum(F_o - k|F_c|)/\sum F_o]$; $R_w = [\sum w(F_o - k|F_c|)^2/\sum wF_o^2]^{1/2}$. [b] esd $= [\sum w(F_o - k|F_c|)^2/(N_{obs} - N_{var})]^{1/2}$; $w = 1/(\sigma(F_o))^2$; $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oL_p$.

Table IV. Bond Distances (Å) and Angles (deg) with Their Esd's in Parentheses for Compounds 3a and 8

Within the $[IrBr_2(CO)_2(CH_2CO_2Me)_2]^-$ Anion			
Ir–Br(1)	2.587 (1)	Ir–Br(2)	2.518 (1)
Ir–C(1)	1.847 (6)	Ir–C(2)	2.038 (7)
Ir–C(11)	2.158 (5)	Ir–C(21)	2.152 (5)
C(1)–O(1)	1.115 (6)	C(2)–O(2)	0.912 (7)
C(11)–C(12)	1.498 (8)	C(21)–C(22)	1.489 (8)
C(12)–O(13)	1.336 (7)	C(22)–O(23)	1.338 (7)
C(12)–O(12)	1.217 (7)	C(22)–O(22)	1.201 (7)
O(13)–C(14)	1.451 (7)	O(23)–C(24)	1.467 (7)
Br(1)–Ir–Br(2)	88.62 (2)	Br(1)–Ir–C(1)	93.3 (2)
C(1)–Ir–C(11)	89.2 (2)	C(11)–Ir–Br(2)	88.7 (2)
Br(1)–Ir–C(2)	86.9 (2)	Br(1)–Ir–C(21)	90.5 (2)
Br(2)–Ir–C(2)	89.3 (2)	Br(2)–Ir–C(21)	85.9 (1)
C(11)–Ir–C(2)	97.2 (2)	C(11)–Ir–C(21)	85.2 (2)
C(1)–Ir–C(2)	92.2 (3)	C(1)–Ir–C(21)	92.7 (2)
Ir–C(1)–O(1)	177.7 (5)	Ir–C(2)–O(2)	177.4 (8)
Ir–C(11)–C(12)	109.5 (4)	Ir–C(21)–C(22)	112.4 (4)
C(11)–C(12)–O(13)	112.2 (5)	C(21)–C(22)–O(23)	113.1 (5)
C(11)–C(12)–O(12)	127.3 (6)	C(21)–C(22)–O(22)	126.0 (6)
O(12)–C(12)–O(13)	120.5 (6)	O(22)–C(22)–O(23)	120.9 (6)
C(12)–O(13)–C(14)	116.4 (5)	C(22)–O(23)–C(24)	116.4 (5)
Within the $[Ir(CO)_2(CH_2CN)_2]^-$ Anion			
Ir–C(1)	1.857 (8)	Ir–C(2)	1.808 (10)
Ir–C(11)	2.142 (8)	Ir–C(21)	2.133 (8)
C(1)–O(1)	1.124 (8)	C(2)–O(2)	1.180 (9)
C(11)–C(12)	1.454 (11)	C(21)–C(22)	1.385 (11)
C(12)–N(13)	1.114 (9)	C(22)–N(23)	1.102 (9)
C(1)–Ir–C(2)	94.3 (4)	C(2)–Ir–C(21)	92.4 (3)
C(21)–Ir–C(11)	83.4 (3)	C(11)–Ir–C(1)	88.9 (3)
Ir–C(11)–C(12)	110.7 (5)	Ir–C(21)–C(22)	120.9 (6)
C(11)–C(12)–N(13)	178.1 (9)	C(21)–C(22)–N(23)	177.9 (10)
Ir–C(1)–O(1)	178.2 (8)	Ir–C(2)–O(2)	177.3 (7)

formed probably by the direct reaction between $PhCH_2Br$ and NaOH.

$[PPN][Ir(CO)_4]$ (1) proved to be less active and less selective than compound 2 as catalyst in this reaction. Negative results were also obtained when $Na[Rh(CO)_4]$ was used as catalyst, in ethanol or isopropyl alcohol as solvent and with $Ca(OH)_2$ as the base, that is, under the conditions for which the $[Co(CO)_4]^-$ anion is a good catalyst for the double carbonylation of benzyl bromide.[11]

Description of the Structures of Compounds 3a and 8. Crystallographic data for **3a** and **8** are given in Table III. Selected bond distances and angles for compounds **3a** and **8** are listed in Table IV. Crystals of both compounds derive from the packing of anions and PPN cations separated by normal van der Waals interactions.

The $[IrBr_2(CO)_2(CH_2COOMe)_2]^-$ anion consists of a hexacoordinated iridium(III) atom, surrounded by two bromines, two carbonyls, and two CH_2COOMe groups, with ligands of the same kind all in cis position. Such a disposition of ligands about the metal center makes it chiral; as the compound crystallizes in the centrosymmetric space group $P\bar{1}$, both the enantiomers with absolute configuration Δ and Λ are packed in the crystal. Figure 1 shows only one of the two enantiomers.

From an inspection of the Ir–Br bond lengths, the different trans influence of the CH_2CO_2Me group with respect to CO is markedly evident. The Ir–C(11) and Ir–C(21) bond lengths are statistically identical, while the Ir–C(2) bond is longer than the Ir–C(1). However this difference is not to be attributable to a different *trans* influence of different substituents but is a consequence of substitutional disorder deriving from a partial replacement of the C(2)O(2) carbonyl with a bromine atom. This fact is not surprising since a 1:1 racemic mixture of the two enantiomers in the crystal would lead to a perfectly ordered situation only if equivalent positions related by translation in the three directions of the cell edges are all occupied by the same enantiomer. If the distribution of the enantiomers in their crystallographic sites is not regular, that is, some of the positions that should have been occupied by one enantiomer are occupied by the one of opposite configuration (situation which, in principle, could not be enthalpically disfavored but is entropically favored), a disordered situation appears, because a bromine atom of one enantiomer lies in the position of a carbonyl ligand of the other and vice versa, the rest of the anion remaining perfectly superimposable, thanks also to the conformational flexibility of the CH_2CO_2Me moieties. As a result also the observed C(2)–O(2) bond length is quite anomalous. Within the CH_2CO_2Me ligands a good agreement is found between corresponding interactions and bond angles. The C(11)–C(12)–O(12)–O(13) and C(21)–C(22)–O(22)–O(23) moieties are planar.

In the $[Ir(CO)_2(CH_2CN)_2]^-$ anion the iridium atom is essentially in a square-planar environment. Of the two CH_2CN ligands one is almost in the coordination plane while the other is normal to the plane. This arrangement

---

(11) Francalanci, F.; Bencini, E.; Gardano, A.; Vicenti, M.; Foà, M. *J. Organomet. Chem.* **1986**, *301*, C27.

is a consequence of the need of preserving normal intramolecular contacts between the ligands. Small differences between corresponding molecular parameters seem to be attributable only to packing effects. The two —C≡N distances are quite short with respect to the usual values found. This shortening is probably an effect of the thermal motion of the C≡N appendages.

Conclusions

The reactions of the $[M(CO)_4]^-$ anions (M = Rh, Ir) with organic halides allowed the isolation or the spectroscopic characterization of new and interesting organometallic derivatives. However their nature is entirely different from that of the compounds observed when using $[Co(CO)_4]^-$ as the complex anion.[12,13] Moreover, while the $[Co(CO)_4]^-$ anion is a good catalyst for the single and double carbonylation of benzyl halides, the $[M(CO)_4]^-$ anions (M = Rh, Ir) gave much poorer results as catalysts in this reaction. In the latter cases, most of the reactions probably proceed via a radical mechanism, which could be due to a greater tendency of rhodium and iridium, with respect to cobalt, to give a homolitic cleavage of the metal–carbon bond, before the insertion of carbon monoxide could occur.

Experimental Section

General Procedure. Unless noted, all reactions and manipulations were carried out under a dinitrogen atmosphere. Solvents used for the synthesis of the complexes and for the catalytic reactions were dried, purified, degassed, and stored under dinitrogen. The starting materials $[PPN][Ir(CO)_4]$ (**1**) and $[PPN][Rh(CO)_4]$ (**2**) were prepared according to literature methods,[14] and they were stored under dinitrogen. The organic reagents are all commercial products and they were used as received.

Infrared spectra were recorded on a Beckman 4210 and on a Nicolet MX-1 FT IR spectrophotometers. ^1H and ^{13}C NMR spectra were recorded on a Brucker VP-80 and on a Bruker AC-200 spectrometers, with TMS as internal standard. Elemental analyses were carried out in the Analytical Laboratories of Milan University. Gas chromatographic analyses were conducted on a Perkin-Elmer 8420 capillary gas chromatograph or on a Dani 8520 gas chromatograph coupled with a Perkin-Elmer Sigma 10B data station.

Preparation of $[PPN][IrBr_2(CO)_2(CH_2CO_2Me)_2]$ (3a). To compound **1** (0.51 g, 0.60 mmol), THF (25 mL) and $BrCH_2CO_2Me$ (0.23 g, 1.5 mmol) were added under a dinitrogen atmosphere. After 3 h the γ_{CO} at 1890 cm^{-1} of the starting material disappeared. The solution was evaporated to dryness in vacuo. The residue was treated with ethyl ether (50 mL), filtered off, and washed with isopropyl alcohol. The white compound was crystallized from chloroform by adding a 80:20 mixture of *n*-hexane and ethyl ether, under a dinitrogen atmosphere (60% yield); mp 115–118 °C; Λ_M = 19.6 Ω^{-1} cm^{-2} mol^{-1} (in $PhNO_2$). Anal. Calcd for $C_{44}H_{40}Br_2IrNO_6P_2$: C, 48.4; H, 3.6; N, 1.3; Br, 14.7. Found: C, 48.2; H, 3.8; N, 1.2; Br, 14.0. Crystals suitable for the X-ray structural determination were obtained by slow diffusion of *n*-hexane into a $CDCl_3$ solution of the complex under a dinitrogen atmosphere. Following this reaction by IR spectroscopy, it was possible to detect the intermediate formation of compound **5a**.

Preparation of $[PPN][IrBr_2(CO)_2(CH_2CN)_2]$ (3b). This compound has been obtained as described for **3a**, by using THF (25 mL), $[PPN][Ir(CO)_4]$ (**1**, 0.51 g, 0.60 mmol), and $BrCH_2CN$ (0.18 g, 1.5 mmol), for 1 h (60% yield); mp 93–95 °C; Λ_M = 22.5 Ω^{-1} cm^{-2} mol^{-1} (in $PhNO_2$). Anal. Calcd for $C_{42}H_{34}Br_2IrN_3O_2P_2$: C, 49.1; H, 3.3; N, 4.1. Found: C, 48.9; H, 3.4; N, 4.0. Following the reaction by IR spectroscopy, it was possible to detect the intermediate formation of **5b**.

Preparation of $[PPN][IrBr_2(CO)_2(CH_2Ph)_2]$ (3c). To compound **1** (0.51 g, 0.60 mmol), THF (25 mL) and $PhCH_2Br$ (0.31 g, 1.8 mmol) were added under a dinitrogen atmosphere. The yellow solution was warmed to 55 °C. After 2.5 h the solution was evaporated to a small volume, and isopropyl alcohol (50 mL) was added, after cooling to 0 °C. The light-brown precipitate was filtered off and washed with isopropyl alcohol (55% yield); mp 83–87 °C; Λ_M = 91 Ω^{-1} cm^{-2} mol^{-1} (in acetone). Anal. Calcd for $C_{52}H_{44}Br_2IrNO_2P_2$: C, 55.3; H, 3.9; N, 1.2. Found: C, 54.5; H, 3.3; N, 1.2. The elemental analysis is not completely satisfactory because compound **3c** contains an impurity of an unknown complex with two infrared absorptions at 2102 and 2044 cm^{-1} in THF (which remain completely unaltered when the complex is reacted with CO) that could not be eliminated. All attempts of recrystallizing **3c** led to decomposition or to the recovery of the nonpurified compound.

Preparation of $[PPN][IrCl_3(CO)_2(COCH_2Ph)]$ (7). a. To a solution of $[PPN][Ir(CO)_4]$ (**1**, 0.55 g, 0.65 mmol) in THF (25 mL), $PhCH_2COCl$ (0.25 g, 1.6 mmol) was added. The solution became orange and then dark yellow. After 3 h a white precipitate (PPNCl) was filtered off and the solution was evaporated to dryness in vacuo. The residue was treated with ethyl ether, and the white compound was filtered off. It was extracted with benzene, filtering off some PPNCl, $[PPN][IrCl_2(CO)_2]$, and a not yet fully characterized cluster compound, and the solution was evaporated to dryness. The yield of this reaction is about 30% but is somewhat variable due to adventitious moisture and reagent impurities.

b. To a solution of $[PPN][IrCl_2(CO)_2]$ (**11**, 0.40 g, 0.47 mmol) in THF (10 mL), $PhCH_2COCl$ (0.44 g, 2.8 mmol) was added. The reaction was followed by IR until the bands of **11** disappeared. The light-yellow solution was evaporated to dryness in vacuo, obtaining an oily residue. It was washed many times with ethyl ether, always drying in vacuo the residue after each washing, until it became a powder (80% yield). Anal. Calcd for $C_{46}H_{37}Cl_3IrNO_3P_2$: C, 54.6; H, 3.7; N, 1.4. Found: C, 54.8; H, 3.8; N, 1.6.

$[PPN][Rh(CO)_4]$ (2) + $BrCH_2R$ → $[PPN][RhBr(CO)_2(CH_2R)]$ (R = COOMe, 4a; R = CN, 4b). About 100 mg of $[PPN][Rh(CO)_4]$ was weighed under dinitrogen in a Schlenk tube and dissolved in 5 mL of THF ($[PPN][Rh(CO)_4]$ is very air sensitive even in the solid state and should never contact air for more than a few seconds.) A 1:1 mole to mole quantity of the organic bromide was then added with a microsyringe. The reaction was almost instantaneous, being complete in a couple of minutes. Both an excess or a defect of organic bromide should be carefully avoided (see the Results and Discussion section). The so-obtained complexes are stable under dinitrogen for some hours. Longer standing, however, causes decomposition to $[RhBr_2(CO)_2]^-$ and other uncharacterized compounds. If a 2:1 mole to mole quantity of organic bromide is used, complete transformation of the intermediately formed **4** to $[RhBr_2(CO)_2]^-$ is observed in 2 h. $[PPN][RhBr_2(CO)_2]$ (**9**) can be isolated in pure form (90% yield) by drying this solution in vacuo and washing the residue with diethyl ether (2 × 10 mL). If a larger quantity of organic bromide is used, the second step of the reaction is quicker, but some $[RhBr_5(CO)]^{2-}$ is also formed. This becomes the dominant product (IR evidence) at large (>10:1) molar ratios of the reactants, although some $[RhBr_2(CO)_2]^-$ is also present in any case.

$[PPN][IrBr_2(CO)_2(CH_2Ph)_2]$ (3c) + 2CO → $[PPN][IrBr_2(CO)_2(COCH_2Ph)_2]$ (6). Compound **3c** (150 mg, 0.13 mmol) was dissolved in THF (3 mL) under a CO atmosphere. The solution was stirred under CO for 1 h, after which time IR evidenced the complete conversion to **6**. The same solution was used to examine the effect of a higher CO pressure (see the Results and Discussion section). Switching the atmosphere from CO to N_2 and bubbling dinitrogen into the solution reversed the reaction. Pure **3c** was reobtained in about 3 h.

$[PPN][IrBr_2(CO)_2(CH_2COOMe)_2]$ (3a) + PPh_3 → $IrBr(CO)(PPh_3)_2$ + CH_3COOMe. $[PPN][IrBr_2(CO)_2(CH_2COOMe)_2]$ (**3a**, 328 mg, 0.3 mmol) and PPh_3 (393 mg, 1.5 mmol) were placed in a 50-mL flask equipped with a reflux condenser, and 18 mL of EtOH was added. The white suspension was heated at reflux for 5 h, during which time the solution turned yellow, and a yellow precipitate was formed. The precipitate was filtered and washed with hot EtOH (30 mL). It was recognized as pure $IrBr(CO)(PPh_3)_2$ (80% isolated yield) by elemental analysis and by comparison of its IR and ^{31}P NMR spectroscopic data with those of

---

(12) Galamb, V.; Palyi, G. *Coord. Chem. Rev.* **1984**, *59*, 203.

(13) (a) Roper, M.; Schieren, M. *J. Organomet. Chem.* **1986**, *299*, 131. (b) Roper, M.; Kruger, C. *J. Organomet. Chem.* **1988**, *399*, 159.

(14) Garlaschelli, L.; Chini, P.; Martinengo, S. *Gazz. Chim. Ital.* **1982**, *112*, 285.

an authentic sample.[10] The presence of methyl acetate was evidenced in the solution by gas chromatographic analysis (packed column Chromosorb 103). No other organic products were observed.

Preparation of $[PPN][Ir(CO)_2(CH_2CN)_2]$ (8). $[PPN][IrBr_2(CO)_2(CH_2CN)_2]$ (**3b**, 0.62 g, 0.60 mmol) was dissolved in THF (30 mL) under a carbon monoxide atmosphere at 0 °C, and a methanolic solution of NaOMe (obtained by dissolving 0.05 g of sodium metal into 10 mL of methanol) was added dropwise until the IR bands of **3b** disappeared. A PPNCl solution (0.6 mmol) in isopropyl alcohol (5 mL) was then added. The solution was evaporated to dryness in vacuo, and the yellow solid was washed with ethyl ether. Crystals of 8 suitable for the X-ray structural determination were obtained by slow diffusion, under carbon monoxide, of *n*-hexane into an acetone solution of 8. Anal. Calcd for $C_{42}H_{34}N_3IrO_2P_2$: C, 58.2; H, 3.9; N, 4.8. Found: C, 58.0; H, 3.9; N, 5.0. Yields of 8 obtained by this way were very low. Higher yields (50%) were obtained by adding to the solution, after the complete disappearance of **3b**, a 50% excess of MeO^- (based on the previously added quantity) and heating it at 40 °C for 2 h. After this time the only product observable in solution by IR is 8. A white precipitate (mostly NaBr) is also formed and is filtered away. Workup is then accomplished as already reported.

Catalytic Reactions. Catalytic reactions under CO pressure were conducted in a glass liner inside a stainless steel autoclave with magnetic stirring. The autoclave was heated by a thermoregulated oil bath. Reagent quantities are given in Table II. $PhCH_2Br$ was charged into the glass liner, which was then placed in a Schlenk tube and cooled by dry ice–acetone. It was then evacuated and dinitrogen was admitted. Then 1 mL of an aqueous solution containing the desired quantity of NaOH was added. Since $[PPN][Rh(CO)_4]$ (**2**) is very air sensitive, it was weighed in excess under dinitrogen and dissolved in THF so that its concentration was 0.010 g/mL. This solution (10 mL) was added to the liner, which was then quickly transferred to the autoclave, which was evacuated and filled with dinitrogen three times. The autoclave was then charged at ambient temperature with the required pressure of carbon monoxide. After the reaction was over the autoclave was cooled by an ice bath and blown off. Hexamethylbenzene (0.1 g) was added to the solution, and 1 mL of this was withdrawn for the gas chromatographic analysis of benzyl bromide. The remaining solution was acidified with HCl to acidic pH. Then 5 mL of water and 15 mL of ethyl ether were added to the solution, and the two phases were separated. Pyridine (2 mL) was added to the ether phase, which was then dried with $CaCl_2$. This solution (2 mL) was silanized with 1 mL of a solution containing 100 mL of bis(trimethylsilyl)acetamide, 100 mL of dry pyridine, and 1 mL of trimethylsilane. The resulting solution was analyzed by gas chromatography with an OV-1 capillary column.

X-ray Data Collection and Structure Determination. Crystal data and other experimental details for compound **3a** and 8 are summarized in Table III. The diffraction experiments were carried out on a Enraf-Nonius CAD-4 diffractometer at room temperature with Mo Kα radiation (λ = 0.710 73 Å). The calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[15] The diffracted intensities were corrected for Lorentz, polarization, and absorption (empirical correction)[16] but not for extinction. Scattering factors and anomalous dispersions corrections for scattering factors of non-hydrogen atoms were taken from ref 17. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares analysis, minimizing the function $\sum w(F_o - k|F_c|)^2$. Anisotropic thermal factors were refined for all non-hydrogen atoms of the anion in compound **3a** and for all non-hydrogen atoms of compound 8. Although all the hydrogen atoms were located from a difference Fourier map, their position was not refined but calculated with C–H = 0.95 Å. The final difference Fourier syntheses showed maxima residuals of 0.4 e/Å^3.

Acknowledgment. We thank the Fondazione G. Donegani for a scholarship to F.R. We also thank Dr. M. Foà for useful discussions and the Progetto Finalizzato Chimica Fine II for financial support.

Registry No. 1, 56557-01-8; **2**, 74364-66-2; **3a**, 125540-48-9; **3b**, 125540-35-4; **3c**, 125519-28-0; **4a**, 125519-32-6; **4b**, 125519-34-8; **5a**, 125519-24-6; **5b**, 125519-26-8; **6**, 125519-36-0; **7**, 125519-30-4; 8, 125519-38-2; **9**, 125540-46-7; 11, 106724-90-7; $BrCH_2CO_2Me$, 96-32-2; $BrCH_2CN$, 590-17-0; $PhCH_2Br$, 100-39-0; $PhCH_2COCl$, 103-80-0; $IrBr(CO)(PPh_3)_2$, 15842-08-7; $PhCH_2COOH$, 103-82-2.

Supplementary Material Available: Atomic coordinates, anisotropic thermal parameters, and calculated positions for hydrogen atoms for **3a** and 8 (8 pages); listings of structure factor amplitudes for compounds **3a** and 8 (65 pages). Ordering information is given on any current masthead page.

---

(15) SDP Plus, Version 1.0, Enraf-Nonius, Delft, The Netherlands, 1980.

(16) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.