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MILD DECARBONYLATION OF TRANSITION METAL CARBONYLS BY RHODIUM(I) COMPLEXES

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Summary

Transition metal carbonyls have been found to react with rhodium(I) complexes under mild conditions with resultant transfer of carbonyl to rhodium. Partial decarbonylation of $Mo(CO)_6$ and $Fe(CO)_5$ gives $Mo(PPh_3)_2(CO)_4$, Mo(Arene)$(CO)_3$ (Arene = benzene, toluene or mesitylene, $Fe(PPh_3)(CO)_4$, $Fe(PPh_3)_2(CO)_3$, Fe(Diene)$(CO)_3$ (Diene = butadiene or isoprene). In the absence of ligands capable of stabilizing partially decarbonylated moieties the decarbonylation goes to completion. In hexamethylphosphoramide the exhaustive decarbonylation of $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$ induced by $[Rh(C_8H_{14})_2Cl]_2$ (C_8H_{14} = cyclooctene) proceeds homogeneously and with retention of the oxidation state of rhodium (+1).

Introduction

In a preliminary communication [1] we described the ligand exchange of molybdenum and tungsten carbonyls with tris(triphenylphosphine)chlororhodium. The formation of mixed complexes $M(PPh_3)(CO)_5$ and $M(PPh_3)_2(CO)_4$, which occurred very readily, was accounted for by the specific affinity of rhodium for carbonyl groups. Further studies [2] revealed that in the absence of ligands capable of stabilizing partially decarbonylated fragments the reaction did not stop at an intermediate stage and complete decarbonylation resulted: metal carbonyls undergo complete loss of carbonyl groups when treated by rhodium—olefin complexes. We have extended our investigations to some other systems and the results are reported here in more detail.

Results and discussion

Recent experiments have demonstrated that the interaction of hexacarbonylmolybdenum and $Rh(PPh_3)_3Cl$ at a Rh/Mo molar ratio 1/1 gives initially pre-

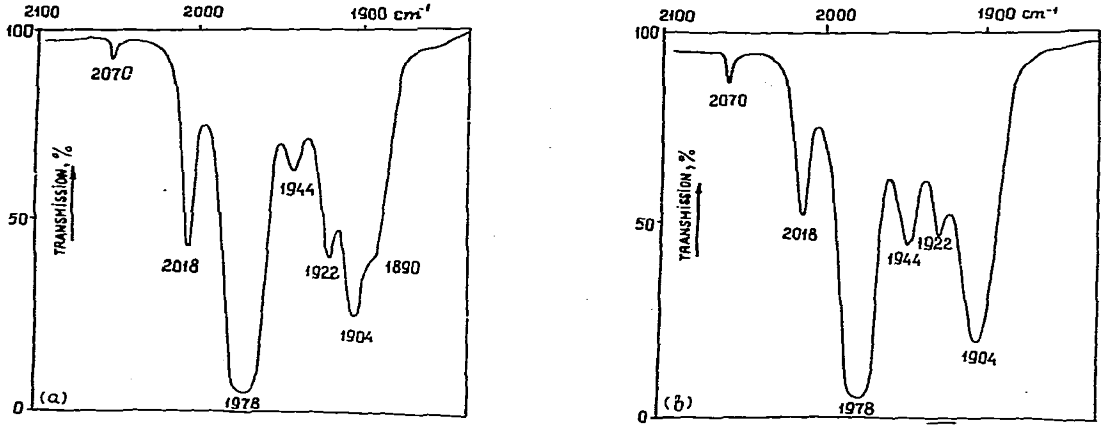

Fig. 1. Infrared absorption spectra of the reaction mixtures of $Mo(CO)_6$ and $Rh(PPh_3)_3Cl$ at Rh/Mo molar ratio 1/1 in toluene at 80°C: (a) after 3 min of reaction; (b) after 30 min.

dominantly *cis*-$Mo(PPh_3)_2(CO)_4$ and also some $Mo(PPh_3)(CO)_5$ (Fig. 1a). We have also observed that a specifically prepared monophosphinepentacarbonylmolybdenum complex does not react with $Rh(PPh_3)_3Cl$ under the conditions used in our studies. These findings may be rationalized according to Scheme 1.

SCHEME 1

$$\begin{tikzcd}
M(CO)_n \arrow[r, "``Rh''"] & M(CO)_{n-1} \arrow[r, "``Rh''"] \arrow[d, "PPh_3"] & M(CO)_{n-2} \arrow[r, "``Rh''"] \arrow[d, "PPh_3"] & \text{etc.} \\
 & M(PPh_3)(CO)_{n-1} & M(PPh_3)_2(CO)_{n-2} &
\end{tikzcd}$$

"Rh" = $Rh(PPh_3)_3ce$

According to this scheme, successive decarbonylation of molybdenum is induced due to attack by the rhodium complex ("horizontal" pathway). The moieties thus formed are stabilized by filling the vacant places with phosphine groups cleaved from rhodium ("vertical" pathway). Since the monophosphine $Mo(CO)_5$ complex does not give up carbonyl groups to rhodium, the $Mo(CO)_5$ moiety apparently loses the second carbonyl group, *cis* to the first one, faster than it adds phosphine. Conversion of $Rh(PPh_3)_3Cl$ is virtually complete within 3 min as estimated from its IR spectra. The subsequent increase in concentrations of *trans*-$Mo(PPh_3)_2(CO)_4$ and $Mo(PPh_3)(CO)_5$ (Fig. 1b) cannot therefore be attributed to further decarbonylation. The final products of the reaction between $Mo(CO)_6$ and $Rh(PPh_3)_3Cl$ are likely to arise from *cis*-$Mo(PPh_3)_2(CO)_4$ by secondary processes, viz. isomerization [3]:

$$cis\text{-}Mo(PPh_3)_2(CO)_4 \rightarrow trans\text{-}Mo(PPh_3)_2(CO)_4$$

and conproportionation, e.g.

$$cis\text{-}Mo(PPh_3)_2(CO)_4 + Mo(CO)_6 \rightarrow 2\ Mo(PPh_3)(CO)_5\ .$$

We actually observed these reactions occurring with *cis*-$Mo(PPh_3)_2(CO)_4$ under the conditions of this study. Decarbonylation also proceeded similarly when the Rh/Mo molar ratio is raised to 2/1,3/1 and 4/1. The quantity of $Rh(PPh_3)_2COCl$ formed in 3 min per mole of $Mo(CO)_6$ amounts to 2, 2.2 and 3 moles respectively. It is interesting to note that even in the latter case the IR spectrum of the reaction mixture did not show the presence of any species containing less than four carbonyl groups although on average the loss of carbonyl groups per molybdenum atom was three. This fact apparently indicates that a portion of the original hexacarbonyl is decarbonylated completely. Notice that the formation of *fac*-$Mo(PPh_3)_3(CO)_3$ by the third "vertical" reaction of Scheme 1 would not be detected since this complex is very easily transformed in solution to *cis*-$Mo(PPh_3)_2(CO)_4$. Specially prepared *fac*-$Mo(PPh_3)_3(CO)_3$ undergoes this reaction with great facility presumably via disproportionation yielding some non-carbonyl molybdenum species as with reactions described in refs. 4 and 5.

The rate of carbonyl exchange between molybdenum and rhodium complexes is considerably slower if an excess of free phosphine is added to the reaction mixture at the start. It seems probable therefore that the dissociation product $Rh(PPh_3)_2Cl$ is more active in decarbonylation than $Rh(PPh)_3Cl$ itself.

The reaction of tris(triphenylphosphine)chlororhodium with hexacarbonyltungsten occurred in a similar manner to that of hexacarbonylmolybdenum. The main product after 3 min at 80° C in toluene is *cis*-$W(PPh_3)_2(CO)_4$ but later *trans*-bisphosphine and monophosphine complexes predominate.

Pentacarbonyliron readily undergoes exchange with tris(triphenylphosphine)chlororhodium (Rh/Fe molar ratio 2/1) at room temperature, yielding $Fe(PPh_3)(CO)_4$, $Fe(PPh_3)_2(CO)_3$ and $Rh(PPh_3)_2COCl$ in agreement with Scheme 1. In this case the monophosphine complex is apparently due to the first "vertical" reaction of Scheme 1, since it was shown conclusively that the bisphosphine complex does not conproportionate with $Fe(CO)_5$ under these experimental conditions. Reaction in chloroform proceeds rapidly and homogeneously (Fig. 2b) with the resulting solution containing $Fe(PPh_3)_2(CO)_3$,

Fig. 2. Infrared absorption spectra of the reaction mixtures of $Fe(CO)_5$ and $Rh(PPh_3)_3Cl$ at Rh/Fe molar ratio 2/1 at room temperature: (a) after 3 h of reaction in benzene; (b) after 5 min of reaction in chloroform.

some $Fe(PPh_3)(CO)_4$ and a small amount of $Fe(CO)_5$, which is absent when the rhodium complex is used in excess ($Rh/Fe \geqslant 3/1$). The rate of pentacarbonyl consumption decreases markedly in the presence of free triphenylphosphine but in 2.5 h the pentacarbonyl is almost quantitatively converted into $Fe(PPh_3)_2(CO)_3$. The product was isolated from the reaction mixture in 85% yield by chromatography on alumina. Reaction in benzene occurred with gradual dissolution of $Rh(PPh_3)_3Cl$ and precipitation of $Rh(PPh_3)_2COCl$. The resulting solution contained comparable amounts of $Fe(PPh_3)(CO)_4$ and $Fe(PPh_3)_2(CO)_3$ and a minor amount of unreacted $Fe(CO)_5$ (Fig. 2a). Preferential formation of $Fe(PPh_3)_2(CO)_3$ suggests that the rates of successive carbonyl abstractions are appreciably reduced once the $Fe(CO)_3$ moiety is formed. It seemed possible therefore, that if the rhodium(I) complexes used for decarbonylation contained ligands other than phosphine, capable of stabilizing the $Fe(CO)_3$ fragment, we should obtain the respective complexes in high yields under mild conditions. This assumption was fully supported in studies of rhodium complexes of conjugated dienes. Quantitative conversion of $Fe(CO)_5$ to $Fe(Diene)(CO)_3$ by $Rh(Diene)_2Cl$ (Diene = butadiene or isoprene) occurred in several minutes in chloroform and in 2.5 h in benzene. The reaction products containing butadiene or isoprene were identified by IR and ^1H NMR spectra.

The reaction between $Fe(CO)_5$ and $Rh(C_4H_6)_2Cl$ is approximately described by the following stoichiometric equation 1:

$$Fe(CO)_5 + 2\,Rh(C_4H_6)_2Cl \rightarrow Fe(C_4H_6)(CO)_3 + \frac{1}{n}[(RhCOCl)_2C_4H_6]_n + 2\,C_4H_6\,. \tag{1}$$

According to eq. 1 carbonylation of rhodium affords a carbonyl complex with a bridging butadiene molecule which has been described elsewhere [6]. The reaction is relatively slow in aliphatic solvents but was used for the convenience of isolating $Fe(C_4H_6)(CO)_3$. Butadienetricarbonyliron can also be prepared by treatment of $Fe(CO)_5$ with mixed Dienecarbonylrhodium complexes: $[(RhCOCl)_2C_4H_6]_n$, $(RhAcac\,CO)_2C_4H_6$ and $(RhOxqCO)_2C_4H_6$ (where AcacH = acetylacetone and OxqH = 8-hydroxyquinoline). The reactions are carried out in benzene or chloroform at room temperature and result in complete conversion of $Fe(CO)_5$ into $Fe(C_4H_6)(CO)_3$. The rhodium complexes yield the well known dicarbonyl derivatives $[Rh(CO)_2Cl]_2$, $RhAcac(CO)_2$ and $RhOxq(CO)_2$.

The IR spectrum of the reaction mixture after treatment of $Fe(CO)_5$ with isoprenerhodium complex, $Rh(C_5H_8)_2Cl$, contained bands of isoprenetricarbonyliron and dicarbonylrhodium complex, $[Rh(CO)_2Cl]_2$. The latter presumably resulted from disproportionation of an initially formed unstable isoprenecarbonylrhodium compound. This assumption is corroborated with our findings on the interaction of isoprene with $[(RhCOCl)_2C_4H_6]_n$ which yielded equal amounts of $[Rh(CO)_2Cl]_2$ and a non-carbonyl isoprenerhodium complex. On addition of cyclooctene to the resulting mixture the coordinated isoprene was replaced by olefin and the complex $[Rh(C_8H_{14})_2Cl]_2$ thus formed conproportionated with $[Rh(CO)_2Cl]_2$ to give $[Rh(C_8H_{14})COCl]_2$ [7]. The yield of final product was quantitative relative to the initial charge of $[(RhCOCl)_2C_4H_6]_n$.

Just as with iron, the molybdenum and tungsten tricarbonyl moieties are also relatively stable towards further decarbonylation. This is evident from the formation of molybdenum and tungsten arenetricarbonyl complexes when the reaction is carried out in aromatic solvent and the decarbonylating reagent is prepared by treating tetraethylene-μ,μ'-dichlorodirhodium(I) with triphenylphosphine (in mole ratio PPh_3/Rh of 1/1). We have utilized this product in situ and tentatively formulate it as $[Rh(PPh_3)C_2H_4Cl]_2$. The decarbonylation of molybdenum and tungsten hexacarbonyls carried out in benzene, toluene and mesitylene resulted in essentially complete transformation of the initial carbonyl to arenetricarbonyl derivatives as shown by IR and ^1H NMR spectroscopy. At 40°C reaction is complete within 30 min; at 80°C in toluene and mesitylene it is complete in 10 min.

The relative inertness of $M(CO)_3$ fragments is presumably due to the fact that the number of remaining carbonyl groups in this moiety is equal to that of the filled d_π-orbitals of the central atom providing the best conditions for π-dative bonding.

A good decarbonylating agent for the removal of all carbonyl groups from a transition metal (exhaustive decarbonylation) turned out to be a cyclooctene-rhodium complex $[Rh(C_8H_{14})_2Cl]_2$. If the process is carried out in benzene at 20°C at a molar ratio of $Rh/M(CO)_n \geqslant n$ the filtrate shows a single carbonyl band at 2003 cm^{-1}, which coincides with that of carbonylcyclooctenerhodium complex $[Rh(C_8H_{14})COCl]_2$. The intensity of the band accounts for 70—85% of the carbonyl groups initially charged. The reaction is accompanied by precipitation of brown intractable solid which contains comparable amounts of both rhodium and the metal from the carbonyl substrate as was found by semi-quantitative estimation from emission spectral analysis. More detailed study of the precipitate was not carried out. The reaction with $Ni(CO)_4$, $Fe(CO)_5$ and $Co_2(CO)_8$ is complete within less than 1 h but with molybdenum and tungsten hexacarbonyls it is considerably slower.

The exhaustive decarbonylation of metal carbonyls in hexamethylphosphoramide (HMPA) solution proceeds homogeneously. $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ were completely decarbonylated in 1—2 h. The IR spectrum of the resulting clear brown-yellow solutions contained a single band in the carbonyl stretching region (1985 cm^{-1}). The position and integral intensity of the band was within the limits of experimental error, identical to that of the reference solution of an equivalent amount of $[Rh(C_8H_{14})COCl]_2$ in HMPA. The addition of PBu_3 both to the reaction mixture and to the reference solution produced a shift of the carbonyl band to 1949 cm^{-1} (Fig. 3) due to formation of $Rh(PBu_3)_2COCl$. The analogous behaviour of $Mo(CO)_6$ and $W(CO)_6$ was also observed in dimethylformamide (DMF).

On the basis of our results the exhaustive decarbonylation may be approximately described by the stoichiometry of eq. 2.

$$\frac{n}{2}[Rh(C_8H_{14})_2Cl]_2 + M(CO)_n \rightarrow \frac{n}{2}[Rh(C_8H_{14})COCl]_2 + \text{“M”} + nC_8H_{14} \qquad (2)$$

We have not yet followed the fate of the decarbonylated metal “M”; that of the cyclooctene replaced by CO in the rhodium complex was observed by means of NMR. In the ^1H NMR spectrum of the reaction mixture ($W(CO)_6 + 3[Rh(C_8H_{14})_2Cl]_2$ in HMPA) (Fig. 3a) the olefinic protons of cyclooctene appeared as a broad resonance at $\delta \sim 5.5$ ppm. The position of the maximum agrees well with that of free cyclooctene

(δ 5.57 ppm) but the signal is unresolved apparently due to exchange with dissolved rhodium complex. Cyclooctene shows a similar broad maximum when added to a HMPA solution of $[Rh(C_8H_{14})COCl]_2$. On addition of PBu_3 to the reaction mixture a well resolved multiplet appears centered at δ 5.57 ppm, which was identical to the —CH=CH—resonance of cyclooctene dissolved in HMPA. The area of the signal was twice that of the previously observed broad resonance. These findings suggest that the cyclooctene when cleaved from rhodium remained virtually uncomplexed in solution.

The exchange between metal carbonyls and tris(triphenylphosphine)chlororhodium proceeds only as far as formation of the monocarbonylrhodium complex $Rh(PPh_3)_2COCl$, however, olefinrhodium complexes may take up two carbonyl groups. Their behaviour in this respect is similar to the relative reactivity of these complexes toward gaseous carbon monoxide. The dicarbonylrhodium species were identified by IR in several cases, e.g. $[Rh(C_8H_{14})_2Cl]_2 + Mo(CO)_6$ in HMPA (Rh/Mo 3/1); $[Rh(C_8H_{14})_2Cl]_2 + Fe(CO)_5$ in HMPA (Rh/Fe 2/1); $[Rh(C_2H_4)_2Cl]_2 + W(CO)_6$ in DMF (Rh/W 3/1); $[RhCODCl]_2 + W(CO)_6$ in HMPA (Rh/W 3/1 and 6/1; COD = 1,5-cyclooctadiene) and $[RhCODCl]_2$ + $Ni(CO)_4$ in HMPA (Rh/Ni 2/1 and 4/1). The precipitate of $RhOxq(CO)_2$ from RhOxqCOD and $Ni(CO)_4$ in benzene (Rh/Ni 2/1) was identified by its IR spectrum and analytical data. Since the cyclooctene complex exchanged both its olefin ligands for carbonyl groups the $[Rh(C_8H_{14})COCl]_2$ may also be used for carbonyl acceptor.

Olefiniridium complexes $[Ir(C_8H_{14})_2Cl]_2$ and $[IrCODCl]_2$ are also active in decarbonylation of metal carbonyls in HMPA or DMF solutions. On adding acetylacetone to the reaction mixture of $Mo(CO)_6 + 1.5[Ir(C_8H_{14})_2Cl]_2$ in HMPA we isolated $IrAcac(CO)_2$ in 65% of theoretical yield.

The evidence obtained is still insufficient to postulate a conclusive mechanism of decarbonylation. Nevertheless, it is reasonable to suggest that the reaction involves nucleophilic attack by the rhodium complex at the carbonyl carbon. Nucleophilic character is endowed to the planar complex by its highest occupied MO's, e.g. $a_1(\sim d_{z^2}$ Rh), $a_2(\sim d_{yz}$Rh) and $b_1(\sim d_{xz}$Rh) in the case of $Rh(PPh_3)_3Cl$ or *trans*-$Rh(PPh_3)_2SCl$ (S = solvent molecule, the x axis goes

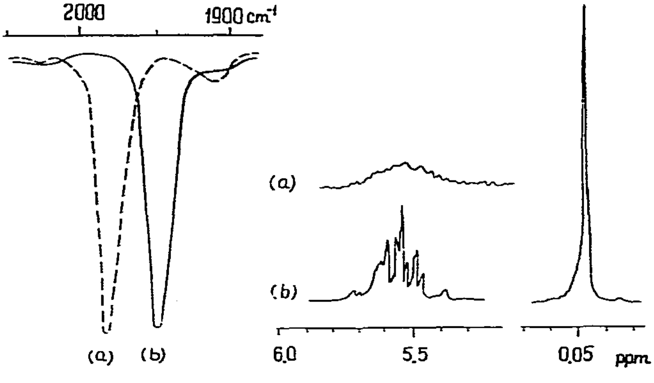

Fig. 3. Infrared and ^1H NMR spectra of the reaction mixture of $W(CO)_6$ and $[Rh(C_8H_{14})_2Cl]_2$ at Rh/W molar ratio 6/1 in HMPA solution (room temperature): (a) before and (b) after addition of excess PBu_3.

through Rh and Cl atoms and the z axis is perpendicular to the plane of the complex [8]). One of these orbitals may interact in a transition state with the antibonding π^*-orbital of the carbonyl group localized on carbon.

Experimental

General

All manipulations were carried out under an atmosphere of dry argon.

Infrared spectra were recorded using Specord-75 IR and IKS-14A spectrometers. The ν(CO) region was calibrated with CO and DCl. Proton magnetic spectra were obtained on Bruker Spectrospin HX-90 and HX-270 instruments utilizing the solvent resonance for internal lock. Chemical shifts were measured from internal hexamethyldisiloxane (δ 0.05 ppm) which eventually served also for intensity checks. They are expressed as δ ppm downfield from tetramethylsilane.

Compounds

Reagent grade transition metal carbonyls were used as received. The following transition metal complexes were prepared by literature methods: *cis*-Mo$(PPh_3)_2(CO)_4$ and *fac*-Mo$(PPh_3)_3(CO)_3$ [9,3]; $Rh(PPh_3)_3Cl$ [10]; $Rh(C_4H_6)_2Cl$ [11]; $Rh(C_5H_8)_2Cl$ [12]; $[Rh(C_8H_{14})_2Cl]_2$, $RhAcac(C_8H_{14})(CO)$ and $RhOxq(C_8H_{14})(CO)$ [7]; $[Rh(C_2H_4)_2Cl]_2$ [13]; $[Rh(COD)Cl]_2$ [14]; $[(RhCOCl)_2C_4H_6]_n$, $(RhAcacCO)_2C_4H_6$ and $(RhOxqCO)_2C_4H_6$ [6]; $[Ir(C_8H_{14})_2Cl]_2$ [15] and arenetricarbonylmolybdenum complexes [16].

Solvents

Benzene, toluene and mesitylene were distilled from calcium hydride under argon. Chloroform and methylene chloride were washed with water, dried over calcium chloride and distilled under argon. Dimethylformamide was distilled under argon from barium oxide. Hexamethylphosphoramide was distilled from molecular sieves in vacuo (110°C, 8 mmHg).

Reactions

$Mo(CO)_6 + Rh(PPh_3)_3Cl$

To a flask containing 15 mg (0.057 mmol) of $Mo(CO)_6$ and 105 mg (0.114 mmol) of $Rh(PPh_3)_3Cl$ (Rh/Mo molar ratio 2/1) was added 1.25 ml of toluene. The reaction mixture was stirred for 3 min at 80°C. The precipitate rapidly changed color from dark red to yellow. The suspension was immediately cooled to room temperature and the resulting precipitate was separated by filtration, washed with toluene (2 X 0.5 ml) and dried in vacuo. IR of the precipitate: ν(CO) 1966 (Nujol mull) or 1978 cm^{-1} ($CHCl_3$) which corresponds to ν(CO) of $Rh(PPh_3)_2COCl$. IR of the filtrate: ν(CO)(cm^{-1}) 2070w, 1944 cm^{-1} corresponding to $Mo(PPh_3)(CO)_5$ and 2018, 1922s, 1904vs, 1888m cm^{-1} corresponding to *cis*-$Mo(PPh_3)_2(CO)_4$. A very strong band at 1976 cm^{-1} is due to the combined absorption of $Mo(CO)_6$ and $Rh(PPh_3)_2COCl$. The reaction proceed similarly at Rh/Mo molar ratio 1/1, 3/1 and 4/1. The estimated yields of $Rh(PPh_3)_2COCl$ from 15 mg of $Mo(CO)_6$ at Rh/Mo $\geqslant 2$ (toluene, 80°C) are given in Table 1.

TABLE 1

Rh/Mo molar ratio	Time (min)	Yield of $Rh(PPh_3)_2CoCl$ (g)	Conversion of $Rh(PPh_3)_3Cl$ (%)
2/1	3	0.074	95
3/1	3	0.086	73.5
4/1	3	0.109	69.5
3/1	10	0.113	96.5
4/1	10	0.139	88.5

In the presence of PPh_3 at $Rh/Mo/PPh_3$ molar ratio of 2/1/1 only 0.051 g of $Rh(PPh_3)_2COCl$ was formed in 3 min (conversion of $Rh(PPh_3)_3Cl$ 66%).

Quantitative estimation of yield of $Rh(PPh_3)_2COCl$

The precipitate separated by filtration after reaction in toluene was washed with toluene (2 × 0.5 ml). The solvent and residual molybdenum hexacarbonyl was carefully removed in vacuo with slight heating. The residue was dissolved in a measured volume of chloroform and the optical density at $\nu(CO)$ band maximum (1978 cm^{-1}) was registered. The concentration was obtained from a calibration plot which was linear within the limits of 5×10^{-4}—10^{-2} mol/l. A correction was made for $Rh(PPh_3)_2COCl$ dissolved in the filtrate (0.004 g per 1.25 ml of the reaction mixture) and washings (0.003 g in 1 ml of toluene). The absence of $Mo(CO)_6$ which absorbs at the same frequency was checked as follows. On addition of excess iodine to an aliquot of solution the maximum for the rhodium complex is displaced to 2088 cm^{-1} because $Rh(PPh_3)_2COClI_2$ is formed. In the absence of $Mo(CO)_6$ no residual absorption was observed at 1980 cm^{-1}.

$Fe(CO)_5$ + $Rh(PPh_3)_3Cl$ at Rh/Fe molar ratio of 2/1

(a) In benzene. 123 mg (0.133 mmol) of $Rh(PPh_3)_3Cl$ was stirred in a solution of 13 mg (0.066 mmol) of $Fe(CO)_5$ in 2 ml of benzene for 3 h at room temperature. The precipitate changed color from dark red to yellow and the solution became reddish orange. The solid was separated by filtration, washed with hexane and dried. The product was identified as $Rh(PPh_3)_2COCl$ by its IR spectrum. IR spectrum of the filtrate, $\nu(CO)$: 2046, 2015w, 1990(sh), 1972, 1935, 1882 cm^{-1}. The bands at 2046 and 1935 cm^{-1} are attributed to $Fe(PPh_3)(CO)_4$, the third band, at 1972 cm^{-1} coincides with that of a rhodium complex. The band at 1882 cm^{-1} belongs to $Fe(PPh_3)_2(CO)_3$. Absorptions at 2015 and 1990 cm^{-1} indicate the presence of some $Fe(CO)_5$.

(b) In chloroform. To a flask containing 123 mg (0.133 mmol) of $Rh(PPh_3)_3Cl$ was added 13 mg (0.066 mmol) of $Fe(CO)_5$ in 2 ml of chloroform. The rhodium complex dissolved immediately yielding a red-orange solution. After 5 min the IR spectrum of the solution contained bands at 2048, 2015w, 1978, 1941, 1883 cm^{-1}. The spectrum recorded after 1 h was unchanged. The bands at 1978 and 1883 cm^{-1} are in agreement with the absorption maxima of $Rh(PPh_3)_2COCl$ and $Fe(PPh_3)_2(CO)_3$ respectively. The bands at 2048, 2015 and 1941 cm^{-1} indicate the presence of $Fe(PPh_3)(CO)_4$ and small amounts of $Fe(CO)_5$ in the reaction mixture.

(c) Isolation of $Fe(PPh_3)_2(CO)_3$. To a flask containing 3.24 g (3.5 mmol) of $Rh(PPh_3)_3Cl$ and 0.92 g (3.5 mmol) of PPh_3 was added 0.342 g (1.75 mmol) of $Fe(CO)_5$ in 28 ml of chloroform. The solution formed was stirred for 2 h at room temperature. The IR spectrum of the resulting mixture contained two strong bands at 1978 and 1883 (see above) and a weak absorption at 2015 cm^{-1} indicative of residual $Fe(CO)_5$. After evaporation of the chloroform in vacuo the residue was extracted with methylene chloride and the remaining yellow solid was washed with a little methylene chloride and hexane and dried to yield 2.37 g (98%) of $Rh(PPh_3)_2COCl$. The product was identified by its IR spectrum and analytical data. The triphenylphosphine, $Fe(PPh_3)_2(CO)_3$ and rhodium complexes contained in the methylene chloride extract were separated by chromatography on alumina. The adsorbent was previously heated under reduced pressure and cooled in an atmosphere of dry argon. The alumina thus prepared was used to pack a column filled with dry hexane. The methylene chloride extract was applied on another portion of adsorbent which was placed on the top of the column. Free triphenylphosphine was eluted with hexane, the main fraction was eluted with a benzene—hexane mixture (1/1 by volume). The yellow eluate was concentrated by evaporation under reduced pressure yielding 0.98 g (85%) of $Fe(PPh_3)_2(CO)_3$ (yellow crystals). The product was identified by its IR spectrum and m.p. 260°C (dec.). Rhodium complexes and other impurities were retained in the column.

$Fe(CO)_5$ + $Rh(C_4H_6)_2Cl$ at Rh/Fe molar ratio 2/1

(a) In chloroform. Dibutadienechlororhodium (53 mg, 0.215 mmol) was added to 21 mg (0.107 mmol) of $Fe(CO)_5$ in 3 ml of chloroform. The rhodium complex dissolved immediately. The IR spectrum recorded after 10 min contained bands at 2050 and 1980 cm^{-1} assigned to $Fe(C_4H_6)(CO)_3$ and a band at 2032 cm^{-1} of $[(RhCOCl)_2C_4H_6]_n$. To an aliquot of the solution was added an excess of triphenylphosphine. The precipitate was separated by filtration. The ^1H NMR spectrum of the filtrate contained three complex multiplets of equal intensity in the 0—6 ppm region at δ 0.24, 1.82 and 5.33 ppm which were assigned to coordinated Diene in $Fe(C_4H_6)(CO)_3$ and a CH_2-resonance of free butadiene centered at 5.14 ppm. The yield of $Fe(C_4H_6)(CO)_3$ was estimated relative to a weighed amount of acetonitrile added to the solution for reference (methyl signal at 1.98 ppm). Conversion of $Fe(CO)_5$ into $Fe(C_4H_6)(CO)_3$ was almost quantitative.

The solvent from another aliquot was evaporated in vacuo after addition of the triphenylphosphine. The solid residue obtained was treated with methylene chloride and dried. The weight of the resulting solid accounted for an almost 100% yield of rhodium carbonyl complex.

(b) Isolation of $Fe(C_4H_6)(CO)_3$. To a solution of 0.32 g (1.63 mmol) of $Fe(CO)_5$ in 15 ml of isopentane was added 0.81 g (3.28 mmol) of $Rh(C_4H_6)_2Cl$. The suspension was stirred at room temperature for 8 h and left overnight. The solution was then filtered. The precipitate (0.60 g) contained mainly $[(RhCOCl)_2C_4H_6]_n$. The filtrate was concentrated in vacuo to yield 0.3 g of an oily product. As demonstrated by ^1H NMR (in chloroform) this product was composed of 60% $Fe(C_4H_6)(CO)_3$ and a considerable amount of isopentane. The material was redissolved in 10 ml of isopentane. The IR spectrum of the result-

ing solution contained strong bands due to $Fe(C_4H_6)(CO)_3$ at 2060, 1992 and 1981 cm^{-1}, weak absorptions at 2091 and 2031 cm^{-1} due to $[Rh(CO)_2Cl]_2$ present as an impurity and very weak bands due to $Fe(CO)_5$. To remove the rhodium complex the isopentane solution was treated with gaseous NH_3. The precipitate of violet colored $Rh(CO)_2NH_3Cl$ (0.03 g) was separated by filtration and the solvent removed under reduced pressure. The butadienetricarbonyliron was sublimed and collected as yellow crystals on a surface cooled by dry ice (0.12 g, 44%). The IR spectrum of the product (as a liquid film between KBr windows) in the 4000—400 cm^{-1} region was in agreement with the literature.

$Fe(CO)_5$ + $Rh(C_5H_8)_2Cl$ at Rh/Fe molar ratio of 2/1

To a solution of 26 mg (0.132 mmol) of $Fe(CO)_5$ in 2 ml of chloroform was added 73 mg (0.264 mmol) of diisoprenechlororhodium. After 10 min the yellow-brown solution was filtered and its IR spectrum registered. The spectrum contained bands due to $Fe(C_5H_8)(CO)_3$ at 2050 and 1980 cm^{-1} together with those of $[Rh(CO)_2Cl]_2$ in the presence of isoprene (2088, 2032(sh), 2015 cm^{-1}; see next section). The absorption assigned to $[Rh(CO)_2Cl]_2$ disappeared on addition of excess tributylphosphine and a band due to $Rh(PBu_3)_2COCl$ appeared at 1949 cm^{-1}. The ^1H NMR spectrum indicated the presence of isoprenetricarbonyliron (complex signals at 0.05, 0.15, 0.36, 1.60, 1.72 and ~5 ppm and a methyl singlet at 2.20 ppm) and some free isoprene (methyl resonance at 1.9 ppm and multiplet at 5 ppm).

The reaction proceeded just as readily in other solvents, e.g. benzene (about 1 h) and occurred in a similar manner at a Rh/Fe molar ratio 1/1. Dienetricarbonyliron complexes are also easily prepared by treating $Fe(CO)_5$ with $[Rh(C_8H_{14})_2Cl]_2$ in liquid isoprene (or butadiene).

$[(RhCOCl)_2C_4H_6]_n$—isoprene interaction

(a). To a flask containing 25 mg of $[(RhCOCl)_2C_4H_6]_n$ was added a mixture of 0.5 ml of isoprene and 0.5 ml of chloroform. After 5 min the solvent was removed in vacuo leaving an oily residue which was dissolved in 1 ml of chloroform. IR spectrum $\nu(CO)$ ($CHCl_3$ solution): 2084, 2050w, 2015 cm^{-1}. The chloroform solution of equimolar quantities of $[Rh(CO)_2Cl]_2$ and $Rh(C_5H_8)_2Cl$ showed two bands in the carbonyl region (2084, 2015 cm^{-1}). IR spectrum of $[Rh(CO)_2Cl]_2$ in chloroform solution contains bands at 2106w, 2088, 2032 cm^{-1}; with some isoprene added bands are at 2088, 2050w, 2032, 2015 cm^{-1} (the relative intensities of the maxima at 2050, 2032 and 2015 cm^{-1} vary slightly).

(b). To 25 mg of $[(RhCOCl)_2C_4H_6]_n$ was added a mixture of 0.5 ml isoprene and 0.5 ml chloroform. The solution was concentrated in vacuo and 1 ml of chloroform and 0.02 ml of cyclooctene added. After 15 min the solvent was evaporated and a further 1 ml of chloroform added. IR spectrum $\nu(CO)$ ($CHCl_3$ solution): 2006 cm^{-1}; the position and integral intensity of the band was identical to that of a reference solution of 36 mg of $[Rh(C_8H_{14})(COCl]_2$ in 1 ml $CHCl_3$.

$Mo(CO)_6$ + $\{[Rh(C_2H_4)_2Cl]_2 + 2PPh_3\}$ at Rh/Mo molar ratio 3/1

(a) In toluene. 33 mg (0.085 mmol) of $[Rh(C_2H_4)_2Cl]_2$ and 45 mg (0.17

mmol) of PPh_3 are stirred for 15 min in 2 ml of toluene. To the suspension was then added 15 mg (0.057 mmol) of $Mo(CO)_6$. After stirring for 10 min at 80° C the reaction mixture was filtered. IR spectrum ν(CO)(filtrate): 1968 and 1888 cm^{-1} ($Mo(C_6H_5Me)(CO)_3$) and 1980(sh) cm^{-1} (assigned to phosphinecarbonylrhodium complex. ^1H NMR: 4.62(t); 4.31(d); 4.27(t) ppm analogous to the spectrum of a specially prepared solution of $Mo(C_6H_5Me)(CO)_3$ in toluene.

(b) In mesitylene. To the suspension obtained as in the previous section from 87 mg (0.33 mmol) PPh_3, 65 mg (0.165 mmol) of $[Rh(C_2H_4)C_2Cl]_2$ and 3 ml of mesitylene was added 29 mg (0.11 mmol) of $Mo(CO)_6$. The reaction mixture was stirred for 5 min at 80° C and than filtered. IR spectrum ν(CO)(filtrate): 1962 and 1884 cm^{-1} ($Mo(C_6H_3Me_3)(CO)_3$) and 1980(sh).cm^{-1} (phosphinecarbonylrhodium complex). ^1H NMR: singlet at 4.27 ppm characteristic of the aromatic protons of mesitylenetricarbonylmolybdenum in toluene solution.

$W(CO)_6$ + $[Rh(C_8H_{14})_2Cl]_2$ in HMPA at Rh/W molar ratio 6/1

390 mg (0.55 mmol) of $[Rh(C_8H_{14})_2Cl]_2$, 63.4 mg (0.18 mmol) $W(CO)_6$ and 7.5 ml of HMPA were stirred for 2 h at room temperature. The IR spectrum of the resulting clear brown-yellow solution contained a single band at 1985 cm^{-1}. The position and integral intensity of the band was within the limits of experimental error, identical to that of a reference solution of 0.55 mmol of $[Rh(C_8H_{14})COCl]_2$ in 7.5 ml of HMPA. The carbonyl absorption shifted to 1949 cm^{-1} on addition of excess PBu_3 to both the reaction mixture and the reference solution. This was due to formation of $Rh(PBu_3)_2COCl$. In ^1H NMR spectrum a broad resonance is observed with maximum at 5.5 ppm. On addition of PBu_3it is transformed into a well resolved multiplet centred at 5.57 ppm due to the olefinic protons of free cyclooctene.

$Fe(CO)_5$ + $[Rh(C_8H_{14})_2Cl]_2$ in HMPA at Rh/Fe molar ratio 5.5/1

To a flask containing 13 mg (0.066 mmol) of $Fe(CO)_5$ were added in succession 2 ml of HMPA and 130 mg (0.181 mmol) of $[Rh(C_8H_{14})_2Cl]_2$. The mixture was stirred for 1 h at room temperature and the resulting red-orange solution was filtered. The single carbonyl band in the IR spectrum of the filtrate (1985 cm^{-1}) was identical in position and integral intensity to that of a reference solution of 0.165 mmol of $[Rh(C_8H_{14})COCl]_2$ in 2 ml of HMPA. The carbonyl absorption maximum is shifted to 1949 cm^{-1} on addition of PBu_3.

$Mo(CO)_6$ + $[Ir(C_8H_{14})_2Cl]_2$ in HMPA at Ir/Mo molar ratio 3/1

A mixture of 269 mg (0.3 mmol) of $[Ir(C_8H_{14})_2Cl]_2$, 53 mg (0.2 mmol) of $Mo(CO)_6$ and 15 ml of HMPA was stirred for 2.5 h at room temperature. The IR spectrum of the resulting clear brown solution contained bands with maxima at 2048,2034, 1967 and 1953 cm^{-1}. On treating the solution in succession with 1 ml of acetylacetone and then ice water, a shining brown precipitate formed. Recrystallization from benzene afforded 140 mg of golden crystals (65% yield of $IrAcac(CO)_2$). The product was identified by its spectrum. (ν(CO) 2075 and 1997 cm^{-1} in CH_2Cl_2).

Identification of reaction products

The reaction products obtained in this study were identified by their respective

IR and ^{1}H NMR spectra using the following literature data: refs. 3, 17 and 18 for $Mo(PPh_3)(CO)_5$, $Mo(PPh_3)_2(CO)_4$ and $Mo(PPh_3)_3(CO)_3$; refs. 19 and 20 for $Fe(PPh_3)(CO)_4$ and $Fe(PPh_3)_2(CO)_3$; refs. 21, 22 and 23 for $Fe(C_4H_6)(CO)_3$; ref. 24 for $Fe(C_5H_8)(CO)_3$; ref. 25 for $IrAcac(CO)_2$ and refs. 26, 27, 28 and 29 for $Mo(C_6H_6)(CO)_3$, $Mo(C_6H_5Me)(CO)_3$ and $Mo(C_6H_3Me_3)(CO)_3$.

The ^{1}H NMR spectra of arenetricarbonylmolybdenum complexes were measured at 270 MHz directly in the reaction mixture, i.e. in excess free arene. The aromatic protons of coordinated toluene in toluenetricarbonylmolybdenum appeared as a triplet at 4.62 ppm) ($2H_{meta}$, J 7 Hz), a doublet at 4.31 ppm ($2H_{ortho}$, J 7 Hz) and a triplet at 4.27 ppm ($1H_{para}$, J 7 Hz) in agreement with the spectrum of a solution of specially prepared $Mo(C_6H_5Me)(CO)_3$ in toluene. It is interesting to note that the phenyl resonances of coordinated toluene are shifted upfield by approximately 1 ppm relative to the same signals of this complex dissolved in chloroform. In chloroform we recorded the corresponding resonances at 5.75, 5.57 and 5.38 ppm and these values are in agreement with literature data. The ^{1}H NMR spectrum of mesitylenetricarbonylmolybdenum in the reaction mixture showed aromatic proton resonance in the same region as for coordinated toluene (singlet at 4.27 ppm).

In order to identify the mixed butadienecarbonylrhodium complex, $[(RhCOCl)_2C_4H_6]_n$, in some of the reactions described above we prepared this compound by two procedures:

(a) Butadiene was condensed onto a surface of solid $[Rh(C_8H_{14})COCl]_2$ (550 mg) cooled to —78°C; 10 ml hexane was added and after 15 min the solution was decanted from the precipitate. Another portion of hexane was added (10 ml) and gaseous butadiene bubbled through the suspension for 15 min. The yellow precipitate was separated by filtration and dried to yield 250 mg of red product.

(b) 246 mg (1 mmol) of $Rh(C_4H_6)_2Cl$ was added to a solution of 194 mg (0.5 mmol) of $[Rh(CO)_2Cl]_2$ in 25 ml of chloroform. The solution immediately changed color from orange to dark red. The ^{1}H NMR of the solution contained a broad signal centred at 5.09 ppm (free butadiene) and resonances at 3.9 and 4.26 ppm with relative areas 1/2 which were assigned to butadienerhodium complex. The IR spectrum contained a single band in the carbonyl region with maximum at 2032 cm^{-1}. The solution was filtered and the solvent removed in vacuo. The solid residue was dried to yield 380 mg of the product.

Both methods gave identical products. Analysis found method (a): Cl, 18.10; Rh, 53.00; method (b): Cl, 18.00; Rh, 53.60. $C_6H_6Cl_2O_2Rh_2$ calcd.: Cl, 18.32; Rh, 53.21%.

We have already published arguments in support of a polymeric structure for the complex [6]. This compound is sparingly soluble in chloroform. Unlike conventional butadiene complexes [30] the ^{1}H NMR spectrum of the complex isolated in our studies did not contain high field signals due to methylene protons (around 0.4 and 2.4 ppm) but only two resonances at 3.9 (1H) and 4.26 (2H) ppm. IR spectrum cm^{-1} (Nujol mull): 498, 532, 564s, 664w, 673w, 693s, 781w, 816, 945(sh), 968s, 1010w, 1024w, 1030(sh), 1204w, 1219w, 1229(sh), 1374w, 1432w, 1454(sh), 1468w, 1472(sh). The carbonyl stretching band maximum in the spectrum of the solid varied slightly from 2038 to 2025 cm^{-1} depending on the sample. In $CHCl_3$ solution ν(CO) is constant at 2032 cm^{-1}.

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