A Facile Route to Carbonylhalogenometal Complexes (M = Rh, Ir, Ru, Pt) by Dimethylformamide Decarbonylation

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Dimethyl formamide (DMF) can be a convenient source of the carbonyl ligand in the coordination chemistry of rhodium, ruthenium, iridium, and platinum. We have undertaken a thorough study concerning the course of this reaction. In a first step, DMF-containing complexes are produced, which is usually accompanied by chloride redistribution. Then, upon refluxing, carbonyl species in the same oxidation state are obtained, presumably as a result of HCl-mediated DMF decomposition. Provided that water levels are kept low, reduction can occur to provide the complexes $[NH_2(CH_3)_2][RhCl_2(CO)_2]$, $[NH_2(CH_3)_2][RuCl_3(CO)_2(DMF)]$, $[RuCl_2(CO)_2(DMF)_2]$, and $[NH_2(CH_3)_2][IrCl_2(CO)_2]$. In the case of platinum, reduction is not effective and $[NH_2(CH_3)_2][PtCl_3(CO)]$ is obtained. No carbonylpalladium species can be synthesized in this way, the reaction producing copious amounts of colloidal metal. Adding phosphanes to these chlorocarbonyl-containing solutions allows easy, one-step syntheses of a variety of complexes.

Introduction

Because of its properties (stable, aprotic, polar, and high boiling point), DMF has been employed as a solvent in a wide variety of catalytic reactions including hydrogenations, hydroformylations, carbonylations, and syn-gas reactions.[1−17] Nevertheless, in some cases, its implication as a reactant has been observed and solvent effects that do not seem to be directly linked with its polarity have been noticed, particularly when the catalytic reaction involves carbon monoxide or further reactions with carbonyl compounds. Thus, in the course of an investigation of the ruthenium-catalyzed hydroesterification of ethylene, the results of which have been reported previously,[1,2] a strong solvent effect was noted. In this reaction, the solvent could be involved in the formation of the active species; in particular, the complex $[PPN][RuCl_3(CO)_2(DMF)]$ has been isolated after reaction of the precatalyst $[PPN][RuCl_3(CO)_3]$ with boiling DMF.[1] In the hydroformylation of formaldehyde using a rhodium catalyst of the general formula $[RhCl(CO)L_2]$ (L: tertiary phosphane ligand), a dramatic effect has been noticed when using DMF as the solvent.[3] This represents an unusual solvent dependence, particularly as the hydroformylation of alkenes can normally be carried out in almost any solvent. The authors postulated that coordination by the solvent could affect the catalyst reactivity. Recently, DMF has been shown to be a ligand of palladium and copper in the course of the oxidation of an alkene to the corresponding ketone.[4] Finally, Mitsudo et al. have developed the direct hydroamidation of alkenes by formamides using ruthenium catalysts.[5] A C−H formyl activation step is invoked in the catalytic cycle.

In the transfer hydrogenation of D-glucose carried out in DMF with $[RuCl_2(PPh_3)_3]$ as a catalyst, a deactivation of the catalyst has been observed.[6,7] At 123 °C, the starting complex was transformed into the catalytically inactive species $[RuCl_2(CO)(DMF)(PPh_3)_2]$, for which the authors assumed that a decarbonylation of the solvent had occurred to generate the carbonyl ligand. In the case of ethylene hydroesterification starting from $RuCl_3{\cdot}xH_2O$, Petit et al.[8] proposed a partial decomposition of DMF to explain the production of $[NMe_4]I$, which involves iodomethane, used to promote the reaction, and dimethylamine produced by DMF decomposition. For the decarbonylation of alkyl formates in the presence of chloride salts of osmium,[9] a positive effect of the solvent has also been noticed. In this case, a catalytic decomposition of DMF to give CO and dimethylamine was proposed; the production of the amine, which can catalyze the decarbonylation of alkyl formates, would seem to provide a good explanation of this effect since formates are usually decomposed in basic media. In this latter study, no information was given regarding the osmium species present at the end of the reaction.

Apart from the aforementioned catalytic reactions, a careful examination of the literature shows that the use of DMF as a carbonylating agent for the synthesis of organometallic compounds has not yet been systematically examined. Even though it has long been known that transition metal salts can give well-characterized carbonyl complexes,

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or in some cases carbonylhydrido complexes, upon treatment with alcohols, acyl halides, aldehydes, or formic acid, little is known about the decarbonylation of DMF. Rusina and Vlćek were the first to report such a reaction,[18] studying the formation of carbonyl complexes of the platinum group metals and using DMF as the CO source. Thus, the complex $[RhCl(CO)(PPh_3)_2]$ was prepared by refluxing a solution of $RhCl_3$ in DMF in the presence of triphenylphosphane. Later, Varshavskii and Cherkasova[19] prepared the acetylacetonato complex $[Rh(acac)(CO)_2]$ by two different routes. The first was similar to that employed by Rusina and Vlćek, involving a one-pot reaction of the salt and acetylacetone in boiling DMF (procedure A). The second route (procedure B) required the prior formation of carbonyl-containing rhodium intermediates obtained by heating $RhCl_3$ in DMF, which were then treated with acetylacetone to give $[Rh(acac)(CO)_2]$. The same group has proposed that in the case of $RhCl_3{\cdot}3H_2O$ and H_2PtCl_6, the $[RhCl_2(CO)_2]^-$ and $[PtCl_3(CO)]^-$ anions, respectively, are produced by DMF decarbonylation.[20] Nevertheless, no explanation was given concerning the course of the reaction.

Since these first synthetic results, other β-diketonato complexes of rhodium have been prepared according to procedure A.[21−24] Vaska's compound $[IrCl(CO)(PPh_3)_2]$ has also been prepared by this procedure.[25] The same method was used to prepare other carbonylphosphane-containing iridium complexes.[26,27] Decarbonylation of DMF has also been used for the preparation of ruthenium species containing bipyridyl ligands of the general formula $[Ru(CO)L(bipy)_2]^{n+}$ starting from $RuCl_3{\cdot}3H_2O$.[28−33] In most of these cases, procedure A is employed and very long reaction times are required. Recently, Forster et al.[34] have reported a 1-h synthesis of the complex $[RuCl(CO)(L{-}L')_2]^+$ (L−L′: pyridyltriazole) using procedure B. The 2-methylimidazole-containing complex *trans*-$[Ru(CO)(DMF)(2\text{-}MeIm)_4][CF_3SO_3]_3$ was synthesized from $[Ru(DMF)_6][CF_3SO_3]_3$ by a reaction involving abstraction of CO from DMF,[35] the required dimethylamine co-product having been detected. The decarbonylation of DMF has also been investigated with the molybdenum complex *trans*-$[Mo(N_2)_2(dppe)_2]$ [dppe: bis(diphenylphosphanyl)ethane] in refluxing benzene.[36] The products of this reaction are the complex $[Mo(CO)(DMF)(dppe)_2]$ and dimethylamine, which was detected by GLC. The authors proposed a mechanism that is exactly the reverse process of the carbonylation of amines by noble metals. The complex $[Mo(CO)(HCONEt_2)(dppe)_2]$ has been similarly prepared starting from diethylformamide. Carbon monoxide and dimethylamine have also been found as the sole products of the decomposition of DMF photocatalyzed by a ruthenium compound containing a porphyrin ligand.[37]

In the course of our investigations on noble metal catalyzed carbonylation reactions, we have undertaken a comprehensive study of the reactions of $RhCl_3{\cdot}3H_2O$, $IrCl_3{\cdot}3H_2O$, $RuCl_3{\cdot}3H_2O$, K_2PtCl_4, $PdCl_2$, and Na_2PdCl_6 with DMF and other amides. Preliminary results of our investigations of the reactions of $RhCl_3{\cdot}3H_2O$ and $IrCl_3{\cdot}3H_2O$ with DMF have already been reported.[38]

Results and Discussion

A. Reaction of $RhCl_3{\cdot}3H_2O$ with DMF

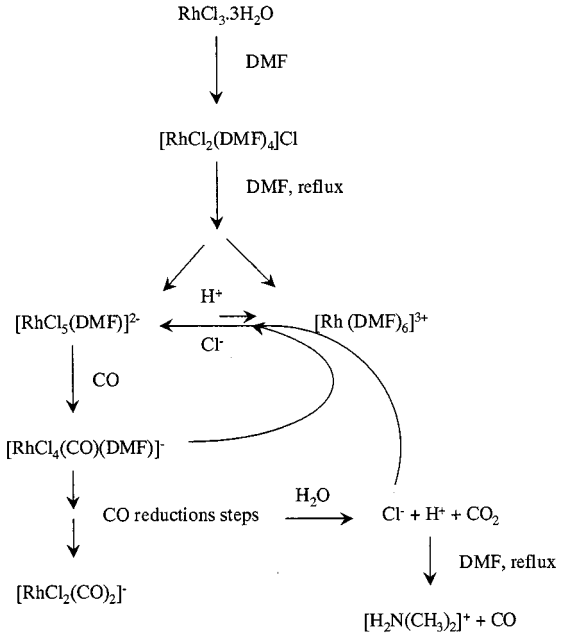
Infrared Monitoring of the Reduction and Identification of Several Intermediate Species

When $RhCl_3{\cdot}3H_2O$ is refluxed in commercially available *N*,*N*-dimethylformamide, the color of the solution changes from dark red to orange within 30 min. If the heating is continued, some metallic rhodium begins to precipitate, indicating a complete reduction of the salt. IR monitoring of the reaction shows that, after 2 min, the dark-red solution contains a carbonyl species at low concentration since a weak carbonyl band is detected at 2092 cm^{-1}. After 5 min, as the solution lightens, two new bands with the same intensity appear beside the band at 2092 cm^{-1}, one at 2063 cm^{-1} and the other at 1984 cm^{-1}. After 15 min, the band at 2092 cm^{-1} has disappeared and only the two strong bands at 2063 and 1984 cm^{-1}, characteristic of the $[RhCl_2(CO)_2]^-$ anion, are present; their intensity remains constant after 30 min of reaction.

Direct evaporation of the solvent from the final orange solution leads to the deposition of large amounts of black insoluble rhodium species along with the complex $[NH_2(CH_3)_2][RhCl_2(CO)_2]$ and the salt $[NH_2(CH_3)_2]Cl$. Alternatively, addition of one molar equivalent of $[AsPh_4]Cl$ affords $[AsPh_4][RhCl_2(CO)_2]$ in 70% yield after recrystallization of the crude product from dichloromethane/*n*-heptane (see Table 1).

In order to identify the first carbonyl intermediate species giving a ν_{CO} band at 2092 cm^{-1}, several experiments were performed that showed this compound to be $[RhCl_4(CO)(DMF)]^-$, as detailed below. A precedent for this anion is the related complex $[RhCl_4(CO)(CH_3OH)]^-$, which gives a ν_{CO} band at 2103 cm^{-1}.[39] This rhodium(III) intermediate is depicted in Scheme 1, together with all the isolated intermediates that can be proposed as being involved in the formation of $[RhCl_2(CO)_2]^-$ from $RhCl_3{\cdot}3H_2O$ through DMF decarbonylation.

In the first of the aforementioned experiments, direct FAB^- mass-spectrometric analysis of the dark-red DMF solution obtained after 2 min revealed only the presence of two main fragments, one at m/z = 245 corresponding to $[RhCl_4]^-$ and the other at m/z = 210 due to $[RhCl_3]^-$. To intercept this first intermediate, 1 mol-equiv. of $[AsPh_4]Cl$ was added to this solution, the solvent was evaporated, and the product was precipitated by adding acetone/*n*-heptane. A reddish powder was obtained, which did not show any carbonyl−rhodium band in its IR spectrum, but rather a broad CO band at 1641 cm^{-1} characteristic of coordinated DMF (free DMF: 1673 cm^{-1}). As mass-spectrometric analysis suggested that chloro-rich species were produced at an early stage of the reaction and that direct isolation of the first carbonyl compound was not possible, probably due to its low concentration and the lability of the CO ligand under our experimental conditions, we investigated the effect of an excess of chloride with regard to the stabilization of



Scheme 1. General reaction pathway for the generation of $[RhCl_2(CO)_2]^-$ from $RhCl_3{\cdot}3H_2O$ and DMF

intermediate species. In the presence of 5−10 mol-equiv. of KCl, rapid precipitation of the violet complex $[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$ was observed upon refluxing $RhCl_3{\cdot}3H_2O$ solutions in DMF. Further heating of the reaction mixture led to the quick re-dissolution of this species, and pure $[AsPh_4][RhCl_2(CO)_2]$ was obtained from the orange solution by adding $[AsPh_4]Cl$ after 25 min of reaction. Therefore, the presence of excess of Cl^- in the medium does not change the outcome of the reaction but allows trapping of $[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$. The corresponding aqua anion $[RhCl_5(H_2O)]^{2-}$ has been reported to be the predominant chlororhodium(III) complex present in hydrochloric acid solutions of $RhCl_3{\cdot}3H_2O$.[26]

In a separate experiment, we carbonylated $[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$ by bubbling CO through a solution in DMF for 15 min at 50 °C. After the addition of $[AsPh_4]Cl$ and evaporation of the solvent, an orange powder was recovered, which analyzed as $[AsPh_4]_2[RhCl_5(CO)]$ and gave a ν_{CO} band at 2081 cm^{-1} (see Table 1). The $[RhCl_5(CO)]^{2-}$ anion has previously been reported by Colton et al. as an intermediate species when $RhCl_3{\cdot}3H_2O$ is treated with hydrochloric and formic acid mixtures to produce $[RhCl_2(CO)_2]^-$.[40] Thus, upon monitoring of the reaction in the absence of CO bubbling, $[RhCl_5(CO)]^{2-}$ is not detected.

We have discovered that reaction of $[AsPh_4]_2[RhCl_5(CO)]$ with 5 equiv. of DMF in boiling chloroform allows isolation of the reddish complex $[AsPh_4][RhCl_4(CO)(DMF)]$ in good yields. This compound shows a ν_{CO} band at 2092 cm^{-1} in DMF.

As these latter anionic species contain more chlorine (five and four Cl ligands, respectively) than the starting rhodium salt, further attempts were made to identify the corresponding cationic complexes, which should presumably have a lower chlorine content. After treating $RhCl_3{\cdot}3H_2O$ with DMF at room temperature for 16 h, we isolated a cationic species that could clearly be formulated as $[RhCl_2(DMF)_4]Cl$. This complex shows one ν_{CO} band at 1639 cm^{-1} (m, broad) in its IR spectrum, which is consistent with a D_{4h} group symmetry, the four coordinated DMF ligands lying in the equatorial plane.

A second cationic complex was isolated as a blue by-product from the $RhCl_3{\cdot}3H_2O$ solution in DMF after heating with an excess of KCl. After 15 min, $[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$ precipitated; after this had been filtered off, the blue species was obtained by slow crystallization from the filtrate. Positive-mode electrospray MS data of the blue material showed that no chloro ligands were present, although the assignment of the more intense peaks at m/z = 280.9, 340.8, 415.0, and 502.8 remains uncertain due to rather facile loss of the coordinated DMF. The presence of one ν_{CO} band at 1655 cm^{-1} in the IR spectrum due to the DMF ligands, and of peaks corresponding to coordinated DMF {in D_2O solution: δ = 7.80 [s, 1 H, $HCON(CH_3)_2$], 2.88 and 2.73 [s, 3 H, $HCON(CH_3)_2$]} in the ^1H NMR spectrum, leads us to propose an $[Rh(DMF)_6]^{3+}$ structure for this complex. The analogous ruthenium complex $[Ru(DMF)_6]^{n+}$ (n = 2, 3) has recently been characterized.[41] This $[Rh(DMF)_6]^{3+}$ complex, for which the counterions are light, as shown by FAB-MS (negative mode), can be formulated as $[Rh(DMF)_6]Cl_3$ and can be expected to react with an excess of Cl^- anions to afford the anionic species $[RhCl_5(DMF)]^{2-}$. The various intermediate cationic rhodium species that have been isolated are reported in Table 1.

It can be concluded from IR monitoring of the reaction and from the isolation or trapping of some of the intermediate species, that the reaction of DMF with the starting rhodium(III) salt involves a complex series of equilibria. The presence of Cl^- ions strongly affects the balance between the identified anionic and cationic species. Both the CO ligand and the $[NH_2(CH_3)_2]^+$ cation arising from DMF have been identified, but no evidence of DMF activation at the metal centre can be given.

Water- and/or HCl-Assisted DMF Activation

A further series of experiments was carried out in order to gain better insight into the parameters that affect the course of the reaction, in particular the role of Cl^- ions. Firstly, the use of commercial DMF, containing around 0.1% of water, produced $[RhCl_2(CO)_2]^-$ in 30 min as an orange solution containing a small amount of black rhodium (Table 2, Figure 1). In each experiment, $[AsPh_4]Cl$ was added and the yield of isolated $[AsPh_4][RhCl_2(CO)_2]$ was determined. In run 1 of Table 2, the yield achieved was 70%.

The addition of chloride (KCl) to the reaction medium stabilizes the system, as shown by the absence of any metallic rhodium, but no significant promoting effect on the reduction was observed (runs 2 and 3 in Table 2). Such an

Table 1. Isolated intermediate rhodium species

Product	Color	IR (ν_{CO} [cm^{-1}]) DMF[c]	KBr pellets	MS[a][b] (*m*/*z*)
$[Rh(DMF)_6]Cl_3$	blue	–	1655	502.8[a]: not assigned
$[RhCl_2(DMF)_4]Cl$	red	–	1639	465[a]: $[RhCl_2(DMF)_4]^+$
$[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$	violet	–	1641	326[a]: $[RhCl_5(NH_2(CH_3)_2)]^-$
$[AsPh_4]_2[RhCl_5(CO)]$	orange	2081	2075	662.8[b]: $[AsPh_4RhCl_5]^-$
$[AsPh_4][RhCl_4(CO)(DMF)]$	reddish	2092	2085, 1637	273[a]: $[RhCl_4(CO)]^-$
$[AsPh_4][RhCl_2(CO)_2]$	yellow	2063, 1984	2054, 1975	229[a]: $[RhCl_2(CO)_2]^-$

[a] FAB. – [b] Electrospray. – [c] Free DMF: 1675 cm^{-1}.

Table 2. Influence of the addition of chloride and/or water on the reaction

(Run number) Formulation[a]	Isolated products (yield), reaction time	Solution colour and comments
(1) $RhCl_3·3H_2O$/DMF	$[AsPh_4][RhCl_2(CO)_2]$ (70%); 30 min	Orange – small amount of black rhodium
(2) $RhCl_3·3H_2O$/5 KCl/DMF	$[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$; 5 min	Orange – no black rhodium
(3) $RhCl_3·3H_2O$/10 KCl/DMF	$[AsPh_4][RhCl_2(CO)_2]$ (72%); 25 min	Orange – no black rhodium
(4) $RhCl_3·3H_2O$/5 HCl/dioxane/DMF	$[AsPh_4][RhCl_2(CO)_2]$ (65%); 45 min	Orange – some black rhodium
(5) $RhCl_3·3H_2O$/10 HCl/dioxane/DMF	Reaction incomplete after 45 min	–
(6) $RhCl_3·3H_2O$/5 HCl/water/DMF	$[AsPh_4][RhCl_2(CO)_2]$ (88%); 12 min	Lemon-yellow – no black rhodium
(7) $RhCl_3·3H_2O$/10 HCl/water/DMF	–	–
(8) $RhCl_3·3H_2O$/5 H_2O/DMF	$[AsPh_4][RhCl_2(CO)_2]$ (85%); 12 min	Lemon-yellow – no black rhodium

[a] $RhCl_3·3H_2O$: 0.2 g (0.75 mmol); DMF: 5 mL; T = 160 °C; subsequent addition of $[AsPh_4]Cl$ for product isolation.

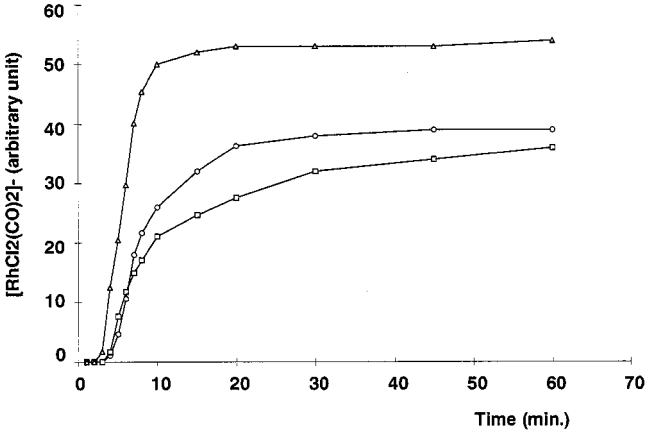


Figure 1. Intensity of the ν_{CO} band of $[RhCl_2(CO)_2]^-$ at 1984 cm^{-1} during the reaction of $RhCl_3·3H_2O$ with: (○) DMF; (□) DMF + 10 mol-equiv. of dry HCl per $RhCl_3·3H_2O$; (△) DMF + 5 mol-equiv. of H_2O per $RhCl_3·3H_2O$

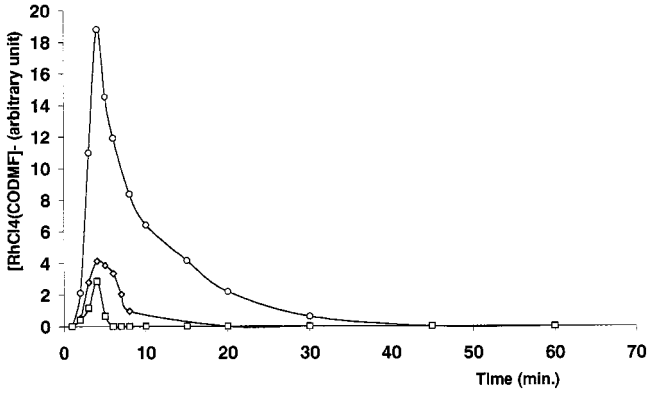


Figure 2. Intensity of the ν_{CO} band of $[RhCl_4(CO)DMF]^-$ at 2092 cm^{-1} during the reaction of $RhCl_3·3H_2O$ with: (○) DMF; (□) DMF + 10 mol-equiv. of dry HCl per $RhCl_3·3H_2O$; (◇) DMF + 5 molar equivalents of H_2O per $RhCl_3·3H_2O$

excess of chloride improved the precipitation of $[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$.

The addition of 5–10 equiv. of dry HCl (5 M HCl in diethyl ether or dioxane) to the $RhCl_3·3H_2O$/DMF mixture was found to have a different and pronounced effect (runs 4 and 5 in Table 2). With 10 equiv., even after reaction for 45 min, the solution remained dark-orange with precipitation of black rhodium. Moreover, the carbonyl band at 2092 cm^{-1} persisted in the IR spectrum (Figures 1 and 2), beside the two bands due to $[RhCl_2(CO)_2]^-$, indicating that the reaction was incomplete. Precipitation of $[NH_2(CH_3)_2]Cl$, arising from DMF decomposition, was also noted. In this case, it is clear from Figure 2 that the production of $[RhCl_4(CO)(DMF)]^-$ was greatly enhanced compared to run 1, suggesting that larger quantities of CO were provided by the acid-catalyzed DMF decomposition. As the yield of $[RhCl_2(CO)_2]^-$ was lower when the concentration of $[RhCl_4(CO)(DMF)]^-$ was significant, we suggest that anhydrous HCl is rapidly neutralized by $NH(CH_3)_2$ arising from the DMF. Thus, no more carbon monoxide can be generated in the medium to maintain the reaction and more particularly the reduction. This experiment further shows that rhodium is unlikely to directly promote the DMF decomposition.

On the contrary, when aqueous solutions of HCl were used (37% in water), another phenomenon was observed; with 5–10 equiv. of acid (runs 6 and 7 in Table 2), the reaction was complete within 12 min and the solution became lemon-yellow, giving the highest yield achieved in this study

(88%). The change in color, i.e. from orange for runs 1 to 5 to lemon-yellow for runs 6 and 7, might be taken to indicate a more complete reaction, as evidenced by the higher yields of the isolated product achieved in the latter cases.

Finally, the role of water itself was examined. We have observed that by adding 5 equiv. of water per mol of rhodium, the reduction can be achieved within 12 min (Table 2, Figure 1 and Figure 2) and the yield of $[RhCl_2(CO)_2]^-$ reaches 85% with no black rhodium formation. We propose that the presence of water assists the reduction step from $[RhCl_4(CO)(DMF)]^-$ to $[RhCl_2(CO)_2]^-$ and that the addition of HCl accelerates the production of CO from DMF, as evidenced by the significant amounts of ammonium chloride detected in the medium. Formally, $COCl_2$ is eliminated in the reduction step and is rapidly hydrolyzed, but we prefer to consider the water-gas shift reaction, which produces CO_2 and H_2 from CO and H_2O. The reduction step is, in fact, the reductive elimination of HCl from the coordination sphere of the rhodium(III) species. Equation (1) shows the overall stoichiometry of several reactions. The complex $[RhI_2(CO)_2]^-$ has previously been shown to be a good catalyst of the water-gas shift reaction.[42]

$$[RhCl_4(CO)(DMF)]^- + 2\,CO + H_2O \rightarrow [RhCl_2(CO)_2]^- + 2\,HCl + CO_2 + DMF \quad (1)$$

To sum up this section on the rhodium activity, we have shown that DMF coordinates to the rhodium salt to give $[RhCl_2(DMF)_4]Cl$, disproportionation of which affords $[RhCl_5(DMF)_2]^{2-}$ and $[Rh(DMF)_6]^{3+}$. The latter species gives the former dianionic one in the presence of chloro ligands. Isolation of $[RhCl_5(DMF)]^{2-}$ with $[NH_2(CH_3)_2]^+$ as the counterion shows that, at this stage of the rhodium(III) chemistry, significant amounts of DMF have been decomposed, thus indicating the presence of an acidic medium. As commercial $RhCl_3{\cdot}3H_2O$ is obtained by evaporation of acidic aqueous solutions of rhodium trichloride, traces of HCl can be present at the beginning of the reaction. However, as no carbonyl species have been detected in the early stages, we conclude that the formation of $[RhCl_2(CO)_2]^-$ resembles an autocatalytic process, which does not involve the activation of DMF at the rhodium center.

Use of Other Amides

In order to test the generality of the reaction, we investigated the behavior of various formamides in this reductive carbonylation. At 180 °C, *N*-methylformamide gave yellow solutions containing a small amount of black material in around 1 min. In their IR spectra, such solutions showed only the two ν_{CO} bands of $[RhCl_2(CO)_2]^-$ at 2073 and 1997 cm^{-1}. The yield of $[AsPh_4][RhCl_2(CO)_2]$ was 72%. When the same reaction was performed at 140 °C, the expected product was obtained in less than 10 min without any precipitation of metallic rhodium. When a solution of $RhCl_3{\cdot}3H_2O$ in formamide was gently heated from room temperature to 120 °C (i.e., well below its boiling point of 210 °C), the ν_{CO} bands of $[NH_4][RhCl_2(CO)_2]$ were detected at 2079 and 2005 cm^{-1} above 100 °C, but the solution was dark and large quantities of black material were deposited. Using diethylformamide at 160 °C produced $[H_2NEt_2][RhCl_2(CO)_2]$ (ν_{CO} = 2060, 1981 cm^{-1}) in 30 min without any metallic precipitate. Although this reaction appeared to be quantitative on the basis of IR measurements, on a small preparative scale the yield of isolated product, usually $[AsPh_4][RhCl_2(CO)_2]$, was ca. 70%. Yields of around 85% were achieved when small quantities of water were introduced to promote the reductive carbonylation. Finally, using *N*-methylacetamide ($CH_3CONHCH_3$; m.p. 28 °C) at 180 °C, a black solution with copious precipitation of a black material was obtained in less than 5 min, and no CO stretching band could be detected in the IR spectrum of the solution.

Direct Preparation of Several Rhodium Complexes

Starting from DMF solutions containing the $[NH_2(CH_3)_2][RhCl_2(CO)_2]$ complex, we added various ligands at room temperature to produce the corresponding rhodium(I) complexes (procedure B). Direct addition of 2 equiv. of PPh_3, as reported by Varshavskii et al.,[19] $P(OPh)_3$, or tris(*m*-sulfonatophenyl)phosphane (TPPTS) furnished the corresponding $[RhCl(CO)L_2]$ square-planar complexes in high yields. Addition of 3 mol of $P(OPh)_3$ resulted in the generation of $[RhCl\{P(OPh)_3\}_3]$. The use of bis(diphenylphosphanyl)propane gave $[Rh(CO)(dppp)_2]Cl$ in 75% yield.

Substitution of the chloro ligand can also be performed. As in the case of $[Rh(acac)(CO)_2]$,[19] addition of 1,1-dimethylethanethiol afforded the corresponding bridged dinuclear complex $[Rh_2(\mu\text{-}S\textit{t}Bu)_2(CO)_4]$ in 80−85% yield. After stirring for 5 min, IR monitoring showed that the tetracarbonyl complex had been formed, and the subsequent addition of 2 equiv. of PPh_3 or TPPTS resulted in the formation of $[Rh_2(\mu\text{-}S\textit{t}Bu)_2(CO)_2(PPh_3)_2]$ or $[Rh_2(\mu\text{-}S\textit{t}Bu)_2(CO)_2(TPPTS)_2]$, respectively.

We have observed that for phosphane ligands, procedure A, in which all the reactants are introduced at the beginning, gives the same results but with much longer reaction times (2−5 h). However, no clean reaction could be achieved by adding HS*t*Bu according to procedure A. Hence, the present method allows the high-yielding preparation in a one-pot procedure of various carbonylrhodium complexes without the use of carbon monoxide gas.

B. Reaction of $IrCl_3{\cdot}3H_2O$ with DMF

An identical study has been carried out on $IrCl_3{\cdot}3H_2O$ in DMF. It is known from the literature[43] that $[IrCl_2(CO)_2]^-$ can be generated using carbon monoxide by refluxing in a high boiling point alcohol such as 2-methoxyethanol. This is presumably due to the higher stability or inertness of iridium(III) compared to rhodium(III).

In the present case, refluxing of a solution of $IrCl_3{\cdot}3H_2O$ in DMF resulted in a beige precipitate after 5 min, which rapidly redissolved on further heating. This species was isol-

ated by stopping the reaction and, after cooling, analyzed as $[NH_2(CH_3)_2]_2[IrCl_5(DMF)]$. As for rhodium, the formation of this species was favored in the presence of an excess of Cl^- ions, for instance in aqueous HCl. After reaction for 10 min, the IR spectrum of the solution showed a ν_{CO} band at 2048 cm^{-1}. The intensity of this band increased, while the color of the solution became progressively more orange. After 30 min, addition of $[AsPh_4]Cl$ to trap this intermediate species resulted in the production of $[AsPh_4][IrCl_4(CO)(DMF)]$, which was isolated as an orange precipitate in 69% yield following the addition of water. On further heating of the initial solution, the two ν_{CO} bands at 2045 and 1965 cm^{-1} intensified, which was accompanied by a concomitant decrease in the band at 2048 cm^{-1}. Heating for 15 h was required to completely transform the starting complex into $[IrCl_2(CO)_2]^-$, albeit with a large amount of black metal. Addition of $[AsPh_4]Cl$ allowed the isolation of $[AsPh_4][IrCl_2(CO)_2]$ in 10% yield.

In order to improve the reduction step from $[IrCl_4(CO)(DMF)]^-$ to $[IrCl_2(CO)_2]^-$, 5 equiv. of water were added. The reaction indeed became faster, but large amounts of the black precipitate were still present. Addition of 5 equiv. of aqueous HCl (37% in water) and heating for 60 min resulted in the clean production of $[IrCl_2(CO)_2]^-$ in 70% yield. Anhydrous HCl or larger amounts of aqueous HCl were found to have a negative effect.

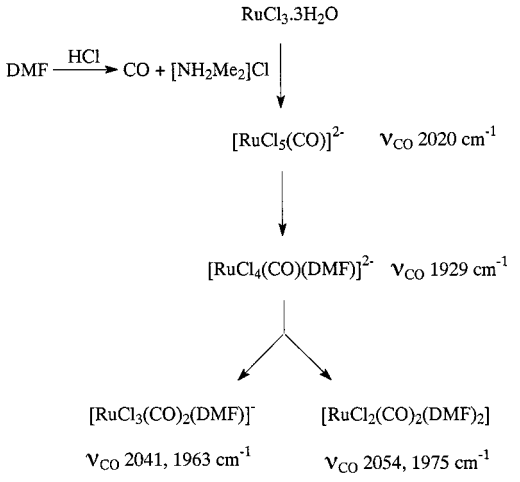
This reaction was thus slower than that for rhodium. The direct isolation of $[IrCl_5(DMF)]^{2-}$ and $[IrCl_4(CO)(DMF)]^-$ indicates that the same mechanism should be operative for both metals. As for rhodium, both the CO ligand and the $[NH_2(CH_3)_2]^+$ cation arising from DMF decomposition could be identified, but again no evidence was found for DMF activation at the metal center.

Addition of 2 equiv. of PPh_3 to the solution containing $[IrCl_2(CO)_2]^-$ was found to result in the immediate formation of $[IrCl(CO)(PPh_3)_2]$. Thus, it appears that procedure B, which involves addition of the ligand after generation of the carbonylchloro anion, is faster than procedure A for generating the desired compound.

C. Reaction of $RuCl_3 \cdot 3H_2O$ with DMF

In the case of ruthenium, the reaction was found to be slower and more complex than that for rhodium. Scheme 2 depicts the various complexes detected during this study.

On heating a solution of $RuCl_3 \cdot 3H_2O$ in DMF, a ν_{CO} band was seen at 2020 cm^{-1} in the IR spectrum after 15 min, corresponding to the red species $[PPN]_2[RuCl_5(CO)]$, which was isolated following the addition of [PPN]Cl. After further heating for 25 min, five more ν_{CO} bands appeared at 2054, 2041, 1975, 1963, and 1929 cm^{-1}. The band at 2020 cm^{-1} rapidly disappeared, whereas that at 1929 cm^{-1} persisted for up to 2 h. The other four bands showed no evolution on heating for longer times. No ruthenium black was observed in the course of the reaction. In a separate experiment, reaction of $RuCl_3 \cdot 3H_2O$ with DMF in the presence of 5 equiv. of aqueous HCl allowed isolation of the green ruthenium(II) product



Scheme 2. General reaction pathway for the generation of $[RuCl_3(CO)_2(DMF)]^-$ and $[RuCl_2(CO)_2(DMF)_2]$ from $RuCl_3 \cdot 3H_2O$ and DMF

$[PPN]_2[RuCl_4(CO)(DMF)]$, showing ν_{CO} bands at 1929 cm^{-1} and 1638 cm^{-1} due to coordinated DMF.

We found that by adding 2.5 equiv. of dry HCl to a solution of $RuCl_3 \cdot 3H_2O$ in DMF, a single complex showing two ν_{CO} bands at 2041 and 1963 cm^{-1} was obtained after reaction for 60 min. In the course of the reaction, the two intermediates giving rise to the bands at 2020 and 1929 cm^{-1} (here shifted to 1919 cm^{-1} due to medium effect) were also transiently observed, but disappeared more quickly. The two final ν_{CO} bands at 2041 and 1963 cm^{-1} are attributable to $[RuCl_3(CO)_2(DMF)]^-$,[1] which was isolated as the PPN salt in 65% yield. Addition of larger amounts of dry HCl resulted in the production of small amounts of $[RuCl_3(CO)_3]^-$ (ν_{CO} bands at 2124, 2008 cm^{-1}), together with $[RuCl_3(CO)_2(DMF)]^-$; this can be attributed to a higher concentration of CO in the solution.

A second complex, showing ν_{CO} bands at 2054 and 1975 cm^{-1}, was isolated following the addition of [PPN]Cl to the yellow solution exhibiting the four ν_{CO} bands at 2054, 2041, 1975, and 1963 cm^{-1} (after refluxing a solution of $RuCl_3 \cdot 3H_2O$ in DMF for 2 h). The products were isolated by precipitation with water. The yellow precipitate was found to contain $[PPN][RuCl_3(CO)_2(DMF)]$ and the unknown complex. Column chromatographic separation on silica allowed isolation of the latter species as pure $[RuCl_2(CO)_2(DMF)_2]$. Scheme 2 summarizes the reaction pathway for the reductive carbonylation of $RuCl_3 \cdot 3H_2O$; it does not involve any DMF activation at the metal center.

As for rhodium and iridium, the solution containing the carbonylchloro species could be used to prepare various complexes. The complex *cis,cis,trans*-$[RuCl_2(CO)_2(PPh_3)_2]$ could be selectively obtained by adding PPh_3 to the solution containing the $[RuCl_3(CO)_2(DMF)]^-$ anion (obtained from a DMF/dry HCl mixture) at 140 °C.

D. Reactions of K_2PtCl_4, $PdCl_2$, and Na_2PdCl_6 with DMF

The reactivities of palladium and platinum salts were found to differ markedly from those of rhodium, iridium,

and ruthenium. Indeed, on refluxing $PdCl_2$ or Na_2PdCl_6 in DMF, the rapid formation of colloidal palladium suspensions was observed within 10 min. Attempts to stabilize possible carbonyl species by adding anhydrous or aqueous HCl, KCl, or even [PPN]Cl, were unsuccessful. Heating a solution of $PdCl_2$ in DMF at 100 °C for 2 h resulted in the formation of a dark solid, which was identified as $[PdCl_2(DMF)_2]$. This compound has already been prepared[44] by treating $PdCl_2$ with DMF at room temperature. However, upon dissolution in another solvent, this complex dissociates with loss of its two DMF ligands. Thus, we did not succeed in finding conditions under which a carbonylpalladium complex could be directly produced from a palladium salt through DMF decarbonylation.

As regards platinum, the refluxing of K_2PtCl_4 in DMF produced copious amounts of black metal. Neither HCl (anhydrous or aqueous) nor KCl prevented this precipitation. Nevertheless, the IR spectrum of the solution showed the presence of a weak ν_{CO} band at 2087 cm^{-1}. Thus, we added 1 equiv. of [PPN]Cl at the beginning of the reaction. Under these conditions, the carbonylplatinum(II) complex [PPN][$PtCl_3(CO)$] could be cleanly obtained without any black precipitate, albeit in a yield of just 52%.

Conclusion

Dimethylformamide, as well as diethylformamide and methylformamide, can act as convenient sources of carbon monoxide. This study has shown that, mainly for rhodium, iridium, and ruthenium, it is possible to produce carbonylhalo complexes in high yields. The presence of small amounts of water clearly assists the reduction of the commercial salts into rhodium(I), $[RhCl_2(CO)_2]^-$, iridium(I) $[IrCl_2(CO)_2]^-$, and ruthenium(II) $[RuCl_4(CO)(DMF)]^{2-}$. Presumably, the reduction proceeds through the water-gas shift reaction. As no evidence has been found for DMF activation at the metal center, an HCl-mediated decomposition of the solvent is proposed to explain the formation of CO and $[NH_2(CH_3)_2]^+$.

The good yields obtained for these carbonyl complexes show that the methodology used in this work is either an attractive one-step route for preparation of the complexes, or a means of directly obtaining the catalytic precursors in DMF solution. Such a procedure is not applicable in the case of palladium, since it leads only to deposition of the black metal, and appears to be limited for platinum, for which $[PtCl_3(CO)]^-$ is obtained in modest yield. Finally, by the direct addition of various ligands to the carbonylhalo-containing DMF solutions, as described here with a few examples, the corresponding classical complexes may be obtained in high yields according to a simplified procedure.

Experimental Section

General Remarks: All synthetic manipulations were carried out under nitrogen using standard Schlenk techniques. Dimethylformamide and the other reagents were used as received (Aldrich). − Elemental analyses were performed with a Carlo Erba EA-1110 instrument. − Infrared spectra were recorded with a Perkin−Elmer 225 spectrophotometer using a 0.1-mm cell equipped with CaF_2 windows. − NMR spectra were recorded with a Bruker AC 200 MHz instrument (^1H, ^{31}P, and ^{13}C). ^1H and ^{13}C NMR spectroscopic data were referenced to the solvent peaks, while ^{31}P NMR spectra were referenced to 85% H_3PO_4 as an external standard. Chemical shifts are expressed in ppm and coupling constants in Hz. − Mass spectrometry (FAB, Xe 100 eV, NBA matrix) was performed with a Nermag R10-10 apparatus. − Procedure B was used for all the syntheses.

Rhodium Complexes

$[NH_2(CH_3)_2]_2[RhCl_5(DMF)]$: The complex was prepared from $RhCl_3{\cdot}3H_2O$ (1.0 g, 3.8 mmol) and KCl (1.41 g, 19 mmol) in DMF (15 mL). On heating the solution under reflux (160 °C) for 15 min, it turned progressively from deep-red to dark-orange and the product precipitated as a violet powder. After cooling to room temperature, the product was collected by filtration using a Büchner funnel, washed with acetone, and dried in vacuo to give 0.255 g (15% based on $RhCl_3{\cdot}3H_2O$). − IR (KBr pellets): ν_{CO} = 1636 cm^{-1} (coordinated DMF). − ^1H NMR (D_2O): δ = 7.81 [s, 1 H, $HCON(CH_3)_2$], 2.88 and 2.73 [2 s, 2 × 3 H, $HCON(CH_3)_2$], 2.60 [s, 6 H, $NH_2(CH_3)_2$]. − $^{13}C\{^1H\}$ NMR (D_2O): δ = 165.2 [d, $HCON(CH_3)_2$, J_{Rh-C} = 17 Hz], 31.4 and 36.9 [s, $HCON(CH_3)_2$], 34.6 [s, $NH_2(CH_3)_2$]. − MS (FAB^-, H_2O): *m/z* (%) = 418 (100) $[\{NH_2(CH_3)_2\}_2\{RhCl_5[HN(CH_3)_2]\}]^-$, 383 (19) $[\{NH_2(CH_3)_2\}_2\{RhCl_4[HN(CH_3)_2]\}]^-$, 326 (26) $[RhCl_5\{HN(CH_3)_2\}]^-$, 244 (31) $[RhCl_4]^-$. − $C_7H_{23}Cl_5N_3ORh$ (445.45): calcd. C 18.87, H 5.20, N 9.43, O 3.59; found C 18.53, H 5.20, N 9.39, O 3.32.

$[AsPh_4][RhCl_4(CO)(DMF)]$: The complex was prepared from $[AsPh_4]_2[RhCl_5(CO)]$ (0.18 g, 0.179 mmol) and DMF (0.065 g, 0.895 mmol) in $CHCl_3$ (10 mL). The solution was heated under reflux for 15 min, allowed to cool, filtered, and the product was precipitated by adding *n*-heptane. It was collected by filtration using a Büchner funnel, washed with *n*-heptane, and dried in vacuo to give 0.11 g {88% based on $[AsPh_4]_2[RhCl_5(CO)]$}. − IR (KBr pellets): ν_{CO} = 2085, 1637 cm^{-1} (coordinated DMF). − ^1H NMR ($CDCl_3$): δ = 7.88 [s, 1 H, $HCON(CH_3)_2$], 2.89 and 2.75 [2 s, 2 × 3 H, $HCON(CH_3)_2$]. − MS (FAB^-, CH_3CN): *m/z* (%) = 362 (10) $[RhCl_4(DMF)]^-$, 289 (100) $[RhCl_4]^-$. − $C_{28}H_{27}AsCl_4NO_2Rh$ (729.17): calcd. C 46.12, H 3.73, N 1.92, O 4.39; found C 45.53, H 3.40, N 1.79, O 4.32.

$[RhCl_2(DMF)_4]Cl$: The complex was prepared from $RhCl_3{\cdot}3H_2O$ (0.5 g, 1.9 mmol) in DMF (15 mL). The solution was stirred at room temperature for 48 h, then filtered, and the solvent was evaporated in vacuo at 50 °C. The resulting oil was treated at room temperature with acetone to yield a brown precipitate. The final product was washed several times with acetone and dried in vacuo to give 0.105 g (11% based on $RhCl_3{\cdot}3H_2O$). − IR (KBr pellets): ν_{CO} = 1639 cm^{-1} (coordinated DMF). − ^1H NMR (D_2O): δ = 8.04 [s, 1 H, $HCON(CH_3)_2$], 2.96 and 2.78 [2 s, 2 × 3 H, $HCON(CH_3)_2$]. − $^{13}C\{^1H\}$ NMR (D_2O): δ = 168.8 [d, $HCON(CH_3)_2$, J_{Rh-C} = 19 Hz], 41.4 and 36.1 [s, $HCON(CH_3)_2$]. − MS (FAB^+, H_2O): *m/z* (%) = 465 (6) $[RhCl_2(DMF)_4]^+$, 392 (5) $[RhCl_2(DMF)_3]^+$, 356 (11.8) $[RhCl(DMF)_3]^+$, 319 (3) $[RhCl_2(DMF)_2]^+$, 248 (100) $[RhCl_2(DMF)]^+$. − $C_{12}H_{28}Cl_3N_4O_4Rh$ (501.64): calcd. C 28.73, H 5.63, N 11.17, O 12.76; found C 28.43, H 5.29, N 10.39, O 11.32.

$[AsPh_4][RhCl_2(CO)_2]$: The complex was prepared from $RhCl_3{\cdot}3H_2O$ (1.0 g, 3.8 mmol) and H_2O (0.35 mL, 19.5 mmol) in

DMF (15 mL). On heating the solution under reflux (160 °C), it turned progressively from deep-red to yellow. IR monitoring indicated the formation of the carbonylchloro anion. After 15 min, $[AsPh_4]Cl$ (1.58 g, 3.8 mmol) was added and the mixture was concentrated to a volume of 3 mL in vacuo at 100 °C. It was then allowed to cool to room temperature and ca. 6 N aq. HCl (20 mL) was added dropwise to precipitate the complex as a yellow powder. The product was collected by filtration using a Büchner funnel, washed with ca. 6 N aq. HCl (100 mL), and dried in vacuo to give 1.98 g (85% based on $RhCl_3 \cdot 3H_2O$). – IR (KBr pellets): ν_{CO} = 2054, 1975 cm^{-1}. – MS (FAB$^-$, CH_3CN): *m/z* (%) = 229 (8) $[RhCl_2(CO)_2]^-$, 201 (16) $[RhCl_2(CO)]^-$, 173 (100) $[RhCl_2]^-$. – $C_{26}H_{20}AsCl_2O_2Rh$ (613.18): calcd. C 50.93, H 3.29; found C 50.62, H 3.27.

[RhCl(CO)L$_2$] Complexes [L = PPh$_3$, P(OPh)$_3$, or TPPTS]: These three compounds were prepared from $RhCl_3 \cdot 3H_2O$ (0.3 g, 1.14 mmol) and H_2O (0.11 mmL, 6.11 mmol) in DMF (10 mL) in a closed Schlenk tube without any reflux condenser system. On heating the solution under reflux, it turned progressively from deep-red to yellow. IR monitoring of the reaction indicated the formation of the carbonylchloro anion $[RhCl_2(CO)_2]^-$. After 15 min, the mixture was cooled to room temperature and 1.95 equiv. of the appropriate phosphane was added [0.58 g of PPh_3, 0.69 g of $P(OPh)_3$ or 1.45 mg of TPPTS]. The reaction was immediate, giving a significant evolution of CO. An IR spectrum of the solution showed a single ν_{CO} band at 1977 cm^{-1} (PPh_3 complex), 2012 cm^{-1} [$P(OPh)_3$ complex], or 1982 cm^{-1} (TPPTS complex). The yellow complexes were precipitated by the addition of cold water (50 mL) [PPh_3 and $P(OPh)_3$ complexes] or ethanol (50 mL) (TPPTS complex). Collection of the products by filtration using a Büchner funnel and washing with water (150 mL) [PPh_3 and $P(OPh)_3$ complexes] or ethanol (150 mL) (TPPTS complex) afforded clean products in reproducible yields of around 80%.

[RhCl(CO)(PPh$_3$)$_2$]: IR (KBr pellets): ν_{CO} = 1960 cm^{-1} (vs). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 32.5 (d, J_{Rh-P} = 125 Hz). – $C_{37}H_{30}ClOP_2Rh$ (690.95): calcd. C 64.32, H 4.38, O 2.32; found C 64.36, H 4.57, O 3.08.

[RhCl(CO){P(OPh)$_3$}$_2$]: IR (KBr pellets): ν_{CO} = 1998 cm^{-1} (vs). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 113.6 (d, J_{Rh-P} = 214 Hz). – $C_{37}H_{30}ClO_7P_2Rh$ (786.95): calcd. C 56.47, H 3.84, O 14.23; found C 56.24, H 4.07, O 14.34.

[RhCl(CO)(TPPTS)$_2$]: IR (KBr pellets): ν_{CO} = 1968 cm^{-1} (vs). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 34.2 (d, J_{Rh-P} = 126 Hz). – $C_{37}H_{36}ClNa_6O_{25}P_2S_6Rh$ (1411.32): calcd. C 31.49, H 2.57, O 28.34; found C 32.12, H 2.63, O 29.68.

[RhCl{P(OPh)$_3$}$_3$]: This compound was prepared by adding 3 equiv. of $P(OPh)_3$ (1.05 g, 3.42 mmol) to the aforementioned $[NH_2(CH_3)_2][RhCl_2(CO)_2]$ solution [prepared from $RhCl_3 \cdot 3H_2O$ (0.3 g, 1.14 mmol) and H_2O (0.35 mL, 19.5 mmol) in DMF (15 mL)] at room temperature. The reaction was immediate, giving a significant evolution of CO. The complex was precipitated by adding cold water (50 mL). Collection of the product by filtration using a Büchner funnel and washing with water (150 mL) afforded a clean product in reproducible yields of around 80%. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 112.5 (dd, J_{Rh-PA} = 222 Hz, J_{PA-PB} = 55 Hz), 118.9 (td, J_{Rh-PB} = 281 Hz, J_{PA-PB} = 55 Hz). – $C_{54}H_{45}ClO_9P_3Rh$ (1069.23): calcd. C 60.66, H 4.24, O 13.47; found C 60.29, H 4.43, O 13.08.

[Rh(CO)(dppp)$_2$]Cl (dppp = 1,3-diphenylphosphanylpropane): This compound was prepared by adding 2 equiv. of dppp (0.94 g, 2.28 mmol) to the aforementioned $[NH_2(CH_3)_2][RhCl_2(CO)_2]$ solution [prepared from $RhCl_3 \cdot 3H_2O$ (0.3 g, 1.14 mmol) and H_2O (0.35 mL, 19.5 mmol) in DMF (15 mL)] at room temperature. The reaction was immediate, giving a significant evolution of CO. The complex was precipitated by adding cold water (50 mL). Collection of the product by filtration using a Büchner funnel and washing with water (150 mL) afforded a clean product in yields of around 70%. – IR (KBr pellets): ν_{CO} = 1930 cm^{-1}. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = –11.8 (td, P_{eq}, J_{Rh-Peq} = 122 Hz, $J_{Peq-Pax}$ = 30 Hz), 16.1 (td, P_{ax}, J_{Rh-Pax} = 85 Hz, $J_{Peq-Pax}$ = 30 Hz) [A_2B_2X]. – ^{31}P-^{103}Rh COSY ($CDCl_3$): δ_{Rh} = 1255. – $C_{55}H_{52}ClOP_4Rh$ (991.27): calcd. C 66.64, H 5.29, O 1.61; found C 66.42, H 4.87, O 1.84.

[Rh$_2$(μ-S*t*Bu)$_2$(CO)$_4$]: This compound was prepared by adding 10 equiv. of 1,1-dimethylethanethiol (900 μL, 11 mmol) to the aforementioned $[NH_2(CH_3)_2][RhCl_2(CO)_2]$ solution [prepared from $RhCl_3 \cdot 3H_2O$ (0.3 g, 1.14 mmol) and H_2O (0.35 mL, 19.5 mmol) in DMF (15 mL)] at room temperature. After 5 min, the IR spectrum of the solution showed four ν_{CO} bands at 2062, 2050, 1999, and 1984 cm^{-1}. The complex was precipitated by the dropwise addition of cold water (50 mL). Collection of the product by filtration using a Büchner funnel and washing with water (150 mL) afforded a clean product in 80–85% yield. – IR (KBr pellets): ν_{CO} = 2060, 2044, 2003, 1990, 1983 cm^{-1}. – $C_{12}H_{18}O_4Rh_2S_2$ (496.22): calcd. C 29.05, H 3.66, O 12.92, S 12.90; found C 28.87, H 3.77, O 12.45, S 12.56.

[Rh$_2$(μ-S*t*Bu)$_2$(CO)$_2$L$_2$] Complexes (L = PPh$_3$ or TPPTS): To the aforementioned solution of $[Rh_2(\mu\text{-}StBu)_2(CO)_4]$ in DMF (see previous synthesis), which exhibited four ν_{CO} bands at 2062, 2050, 1999, and 1984 cm^{-1}, 1 equiv. of the appropriate phosphane per mol of rhodium was added (0.3 g of PPh_3 or 0.73 g of TPPTS). An immediate evolution of CO was noticed and the reaction was complete within 5 min. The IR spectrum of the solution showed a ν_{CO} band at 1977 cm^{-1} (PPh_3 complex) or 1982 cm^{-1} (TPPTS complex). The complex was precipitated by adding cold water (50 mL) (PPh_3 complex) or ethanol (50 mL) (TPPTS complex). Collection of the product by filtration using a Büchner funnel and washing with water (150 mL) (PPh_3 complex) or ethanol (150 mL) (TPPTS complex) afforded clean products in reproducible yields of around 80%.

[Rh$_2$(μ-S*t*Bu)$_2$(CO)$_2$(PPh$_3$)$_2$]: IR (KBr pellets): ν_{CO} = 1964, 1948 cm^{-1}. – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 37.5 (d, J_{Rh-P} = 151 Hz). – $C_{26}H_{20}O_2P_2Rh_2S_2$ (964): calcd. C 56.91, H 5.57, O 3.30, S 6.60; found C 56.81, H 5.51, O 3.20, S 6.38.

[Rh$_2$(μ-S*t*Bu)$_2$(CO)$_2$(TPPTS·3H$_2$O)$_2$]: IR (KBr pellets): ν_{CO} = 1967 cm^{-1}. – $^{31}P\{^1H\}$ NMR (D_2O): δ = 39.7 (d, J_{Rh-P} = 152 Hz). – $C_{46}H_{54}O_{26}Na_6P_2Rh_2S_8$ (1685.14): calcd. C 32.79, H 3.23, O 24.69; found C 33.24, H 3.25, O 25.41.

Iridium Complexes

[NH$_2$(CH$_3$)$_2$]$_2$[IrCl$_5$(DMF)]: The complex was prepared from $IrCl_3 \cdot 3H_2O$ (0.5 g, 1.42 mmol) and aqueous HCl (37%, 250 μL) in DMF (5 mL). On heating the solution under reflux (160 °C), it turned progressively from deep-red to dark-orange and the product precipitated as a beige powder. After 6 min, the mixture was allowed to cool to room temperature and the product was collected by filtration using a Büchner funnel, washed with acetone, and dried in vacuo to give 0.155 g (20% based on $IrCl_3 \cdot 3H_2O$). – IR (KBr pellets): ν_{CO} = 1645 cm^{-1} (coordinated DMF). – ^1H NMR (D_2O): δ = 7.99 [s, 1 H, *H*CON(CH_3)$_2$], 3.07 and 2.98 [2 s, 2 × 3 H, HCON(C*H*$_3$)$_2$], 2.63 [s, 6 H, NH_2(C*H*$_3$)$_2$]. – $^{13}C\{^1H\}$ NMR (D_2O): δ = 174.4 [d, H*C*ON(CH_3)$_2$, J_{Rh-C} = 16 Hz], 35.8 and 40.8

[s, $HCON(CH_3)_2$], 37.4 [s, $NH_2(CH_3)_2$]. − $C_7H_{23}Cl_5IrN_3O$ (534.76): calcd. C 15.72, H 4.34, N 7.86, O 2.99; found C 15.77, H 4.23, N 7.63, O 3.60.

[AsPh$_4$][IrCl$_4$(CO)(DMF)]: The complex was prepared from $IrCl_3 \cdot 3H_2O$ (0.5 g, 1.42 mmol) in DMF (5 mL). On heating the solution under reflux (160 °C), it turned progressively from deep-red to orange. After 30 min, the heating was stopped and [AsPh$_4$]Cl (0.6 g, 1.43 mmol) was added. The mixture was concentrated to a volume of 2 mL and the pale-yellow complex was precipitated by the addition of cold water (25 mL), washed with water (50 mL), and dried in vacuo to give 302 mg (26% based on $IrCl_3 \cdot 3H_2O$). − IR (KBr pellets): ν_{CO} = 2060, 1645 cm^{-1} (coordinated DMF). − ^{1}H NMR ($CDCl_3$): δ = 8.53 [s, 1 H, $HCON(CH_3)_2$], 3.02 and 2.98 [2 s, 2 × 3 H, $HCON(CH_3)_2$]. − MS (FAB$^-$, CH_3CN): *m*/*z* (%) = 405 (100) $[IrCl_4(DMF)]^-$, 362 (12) $[IrCl_4(CO)]^-$, 337 (25) $[IrCl_4]^-$. − $C_{28}H_{27}AsCl_4IrNO_2$ (818.48): calcd. C 41.09, H 3.32, N 1.71, O 3.91; found C 40.86, H 3.33, N 1.78, O 2.75.

[AsPh$_4$][IrCl$_2$(CO)$_2$]: The complex was prepared from $IrCl_3 \cdot 3H_2O$ (0.3 g, 0.85 mmol) and HCl (0.15 mL, 37% in water) in DMF (10 mL). On heating the solution under reflux, it turned from red to orange. After 50 min, HCl (0.10 mL, 37% in water) was added and refluxing was maintained for a further 10 min. Thereafter, the solution was allowed to cool to room temperature and [AsPh$_4$]Cl (0.355 g, 0.85 mmol) was added. After evaporation of the solvent, the complex was washed with acetone/diethyl ether (1:9) to furnish 0.42 g of yellow crystals (71% based on $IrCl_3 \cdot 3H_2O$). − IR (KBr pellets): ν_{CO} = 2036, 1967 cm^{-1}. − MS (FAB$^-$, CH_3CN): *m*/*z* (%) = 319 (19) $[IrCl_2(CO)_2]^-$, 291 (100) $[IrCl_2(CO)]^-$. − $C_{26}H_{20}AsCl_2IrO_2$ (702.49): calcd. C 44.45, H 2.87, O 4.56; found C 44.62, H 2.98, O 4.34.

[IrCl(CO)(PPh$_3$)$_2$]: The complex was prepared by adding 2 equiv. of PPh_3 (0.89 g, 3.4 mmol) to the aforementioned $[NH_2(CH_3)_2][IrCl_2(CO)_2]$ solution in DMF [prepared from $IrCl_3 \cdot 3H_2O$ (0.6 g, 3.8 mmol) and HCl (0.35 mL, 37% in water) in DMF (15 mL)] at room temperature. The reaction was immediate and the IR spectrum of the solution showed a single ν_{CO} band at 1965 cm^{-1}. The lemon-yellow complex was then precipitated by adding cold water (100 mL), collected by filtration using a Büchner funnel, and washed with cold methanol (100 mL). After drying in vacuo, 1.59 g of $[IrCl(CO)(PPh_3)_2]$ was collected (60% based on $IrCl_3 \cdot 3H_2O$). − IR (KBr pellets): ν_{CO} = 1957 cm^{-1}. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 24.1 (s). − $C_{37}H_{30}ClIrOP_2$ (780.27): calcd. C 56.96, H 3.88, O 2.05; found C 56.62, H 4.27, O 3.34.

Ruthenium Complexes

[PPN]$_2$[RuCl$_5$(CO)]: The complex was prepared from $RuCl_3 \cdot 3H_2O$ (0.4 g, 1.53 mmol) in DMF (15 mL) in a closed Schlenk tube without any reflux condenser system. The solution was heated under reflux and IR monitoring of the reaction showed the formation of the carbonylchloro anion (ν_{CO} = 2020 cm^{-1}). After 10 min, the solution was allowed to cool and [PPN]Cl (0.88 g, 1.53 mmol) was added. After concentration of the solution in vacuo at 100 °C to a volume of 5 mL, cold water (10 mL) was added dropwise to precipitate the complex as a dark-red powder. After collection of the product by filtration using a Büchner funnel and washing with water (100 mL), the product was dried in vacuo to give 0.15 g (7% based on $RuCl_3 \cdot 3H_2O$). − IR (KBr pellets): ν_{CO} = 2008 cm^{-1}. − $C_{73}H_{60}Cl_5N_2OP_4Ru$ (1383.52): calcd. C 63.37, H 4.37, N 2.02, O 1.16; found C 63.22, H 4.33, N 2.18, O 1.55.

[PPN]$_2$[RuCl$_4$(CO)(DMF)]: The complex was prepared from $RuCl_3 \cdot 3H_2O$ (0.3 g, 1.15 mmol) and HCl (250 μL, 37% in water) in DMF (8 mL) in a closed Schlenk tube without any reflux condenser system. On heating the solution under reflux (160 °C), it turned progressively from deep-red to dark-green. After 30 min, the heating was stopped and [PPN]Cl (0.4 g, 0.7 mmol) was added. The green complex was precipitated by adding cold water (25 mL), washed with further water (50 mL), and dried in vacuo to give 0.138 g (26% based on $RuCl_3 \cdot 3H_2O$). − IR (KBr pellets): ν_{CO} = 1918, 1644 cm^{-1} (coordinated DMF). − ^{1}H NMR (CD_2Cl_2): δ = 8.61 [s, 1 H, $HCON(CH_3)_2$], 2.98 and 2.95 [2 s, 2 × 3 H, $HCON(CH_3)_2$]. − $C_{76}H_{67}Cl_4N_3O_2P_4Ru$ (1421.16): calcd. C 64.23, H 4.75, N 2.96, O 2.25; found C 64.32, H 4.52, N 2.38, O 1.86.

[PPN][RuCl$_3$(CO)$_2$(DMF)]: The complex was prepared from $RuCl_3 \cdot 3H_2O$ (0.4 g, 1.53 mmol) and anhydrous 4 M HCl in dioxane (1 mL, 4 mmol) in DMF (15 mL) in a closed Schlenk tube without any reflux condenser system. On refluxing the solution, it turned progressively from red to orange. IR monitoring indicated the formation of the carbonylchloro anion (ν_{CO} = 2042 and 1964 cm^{-1}). After 1 h, the solution was allowed to cool and [PPN]Cl (0.88 g, 1.53 mmol) was added. After concentration of the mixture in vacuo at 100 °C to a volume of 5 mL, cold water (10 mL) was added dropwise to precipitate the complex as a yellow powder. The product was collected by filtration using a Büchner funnel, washed with water (100 mL), dried in vacuo, and recrystallized from acetone/heptane to give 0.85 g of yellow crystals (64% based on $RuCl_3 \cdot 3H_2O$). − IR (KBr pellets): ν_{CO} = 2045, 1970, 1636 cm^{-1} (coordinated DMF). − ^{1}H NMR ($CDCl_3$): δ = 8.52 [s, 1 H, $HCON(CH_3)_2$], 2.91 [s, 6 H, $HCON(CH_3)_2$]. − MS (FAB$^-$, CH_3CN): *m*/*z* (%) = 300 (100) $[RuCl_3(CO)(DMF)]^-$, 280.5 (19) $[RuCl_3(DMF)]^-$, 264.8 (7) $[RuCl_3(CO)_2]^-$, 208 (31) $[RuCl_3]^-$. − $C_{41}H_{37}Cl_3N_2O_3P_2Ru$ (875.13): calcd. C 56.27, H 4.26, N 3.20, O 5.48; found C 56.62, H 4.27, N 3.05, O 5.34.

[RuCl$_2$(CO)$_2$(DMF)$_2$]: The complex was prepared from $RuCl_3 \cdot 3H_2O$ (0.4 g, 1.53 mmol) in DMF (15 mL) in a closed Schlenk tube without any reflux condenser system. On refluxing the solution, it turned progressively from red to orange. After 2 h, it was allowed to cool and [PPN]Cl (0.88 g, 1.53 mmol) was added. After concentration of the mixture in vacuo at 100 °C to a volume of 5 mL, cold water (10 mL) was added dropwise to precipitate a yellow powder. The product was collected by filtration using a Büchner funnel, washed with water (100 mL), and dried in vacuo. Chromatographic separation on a column of silica [Degussa Sipernat 22; eluent: acetone/2-propanol (20:80, v/v)] furnished the pure complex in the first fraction; yield 0.17 g (30% based on $RuCl_3 \cdot 3H_2O$). − IR ($CHCl_3$): ν_{CO} = 2073, 2009, 1652, 1645 cm^{-1} (coordinated DMF). − ^{1}H NMR ($CDCl_3$): δ = 8.28 [s, 1 H, $HCON(CH_3)_2$], 8.37 [s, 1 H, $HCON(CH_3)_2$], 3.18 [s, 3 H, $HCON(CH_3)_2$], 3.16 [s, 3 H, $HCON(CH_3)_2$], 3.06 [s, 3 H, $HCON(CH_3)_2$], 3.00 [s, 3 H, $HCON(CH_3)_2$]. − $C_8H_{14}Cl_2N_2O_4Ru$ (374.19): calcd. C 25.68, H 3.77, N 7.49, O 17.10; found C 25.58, H 3.11, N 6.92, O 16.45.

***cis*,*cis*,*trans*-[RuCl$_2$(CO)$_2$(PPh$_3$)$_2$]:** The complex was prepared by adding 2 equiv. of PPh_3 (0.8 g, 3.05 mmol) to the aforementioned $[NH_2(CH_3)_2][RuCl_3(CO)_2(DMF)]$ solution in DMF [prepared from $RuCl_3 \cdot 3H_2O$ (0.4 g, 1.53 mmol) and anhydrous HCl (1 mL, 4 mmol, 4 M in dioxane) in DMF (15 mL)] at 140 °C. The solution was maintained at this temperature until its IR spectrum showed the ν_{CO} bands at 2058 and 1994 cm^{-1} characteristic of *cis*,*cis*,*trans*-$[RuCl_2(CO)_2(PPh_3)_2]$ (1 h). The yellow solution was then allowed to cool to room temperature, and the pale-yellow complex was precipitated by adding cold water. It was collected by filtration using a Büchner funnel, washed with water (100 mL), and dried in vacuo to give 0.7 g of the title compound (64% based on $RuCl_3 \cdot 3H_2O$).

− IR (KBr pellets): ν_{CO} = 2054, 1992 cm^{-1}. − $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 17.2 (s). − $C_{38}H_{30}Cl_2O_2P_2Ru$ (752.58): calcd. C 60.65, H 4.02, O 4.25; found C 60.85, H 4.15, O 4.94.

Palladium and Platinum Complexes

[$PdCl_2(DMF)_2$]: The complex was prepared from $PdCl_2$ (0.2 g, 1.13 mmol) in DMF (15 mL). The solution was heated for 120 min at 100 °C and then concentrated to dryness in vacuo at 50 °C. The complex (0.091 g, 25% based on $PdCl_2$) was recovered as a black powder. − IR (KBr pellets): ν_{CO} = 1656 cm^{-1} (coordinated DMF). − $C_6H_{14}Cl_2N_2O_2Pd$ (323.52): calcd. C 22.28, H 4.36, N 8.66; found C 22.50, H 3.91, N 7.90.

[PPN][$PtCl_3(CO)$]: The complex was prepared from K_2PtCl_4 (0.4 g, 0.96 mmol) and [PPN]Cl (0.554 g, 0.97 mmol) in DMF (15 mL). The solution was refluxed for 120 min and then allowed to cool to room temperature. The complex (0.438 g, 53% based on K_2PtCl_4) was recovered by precipitation with cold water and washed with further water (100 mL). − IR (KBr pellets): ν_{CO} = 2072 cm^{-1}. − $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 150.2 (s). − $C_{37}H_{30}Cl_3NOP_2Pt$ (868.04): calcd. C 51.20, H 3.48, N 1.61; found C 51.89, H 3.77, N 2.14.

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[1] N. Lugan, G. Lavigne, J. M. Soulié, S. Fabre, Ph. Kalck, J. Y. Saillard, J. F. Halet, *Organometallics* **1995**, *14*, 1712.
[2] S. Fabre, Ph. Kalck, G. Lavigne, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1092.
[3] A. Spencer, *J. Organomet. Chem.* **1980**, *194*, 113.
[4] T. Hosokawa, T. Nomura, S. I. Murahaschi, *J. Organomet. Chem.* **1998**, *55*, 387.
[5] T. Kondo, T. Okada, T. A. Mitsudo, *Organometallics* **1999**, *18*, 4123.
[6] S. Rajagopal, S. Vancheesan, J. Rajaram, J. C. Kuriacose, *J. Mol. Catal.* **1983**, *22*, 131.
[7] S. Rajagopal, S. Vancheesan, J. Rajaram, J. C. Kuriacose, *J. Mol. Catal.* **1983**, *22*, 137.
[8] C. Legrand, Y. Castanet, A. Mortreux, F. Petit, *J. Chem. Soc., Chem. Commun.* **1994**, 1173.
[9] C. Legrand, Y. Castanet, A. Mortreux, F. Petit, *Tetrahedron Lett.* **1992**, *33*, 3753.
[10] T. A. Mitsudo, N. Suzuki, T. Kondo, Y. Watanabe, *J. Org. Chem.* **1994**, *59*, 7759.
[11] F. Ramirez Vega, J. C. Clément, H. des Abbeyes, *Tetrahedron Lett.* **1993**, *34*, 8117.
[12] T. Hayashi, F. Abe, T. Sakakura, M. Tanaka, *J. Mol. Catal.* **1990**, *58*, 165.
[13] T. Hayashi, Z. Hui Gu, T. Sakakura, M. Tanaka, *J. Organomet. Chem.* **1988**, *352*, 373.
[14] G. Süss-Fink, G. F. Schmidt, *J. Mol. Catal.* **1987**, *42*, 361.
[15] G. Süss-Fink, J. Reiner, *J. Mol. Catal.* **1982**, *16*, 231.
[16] G. Süss-Fink, *J. Organomet. Chem.* **1980**, *193*, C20.
[17] P. Isnard, B. Denise, R. P. A. Sneeden, *J. Organomet. Chem.* **1983**, *256*, 135.
[18] A. Rusina, A. A. Vlćek, *Nature* **1965**, *206*, 295.
[19] Y. Varshavskii, T. G. Cherkasova, *Russ. J. Inorg. Chem. Int. Ed. Engl.* **1967**, *12*, 899.
[20] Y. Varshavskii, N. V. Kiseleva, T. G. Cherkasova, N. A. Busina, *J. Organomet. Chem.* **1971**, *31*, 119.
[21] E. Kwaskowska-Chec, J. J. Ziokowski, *Transition Met. Chem.* **1983**, *8*, 103.
[22] E. Kwaskowska-Chec, J. J. Ziokowski, *Transition Met. Chem.* **1991**, *16*, 212.
[23] F. Bonati, L. A. Oro, M. T. Pinillos, *Polyhedron* **1985**, *4*, 357.
[24] A. M. Trzeciak, J. J. Ziokowski, *Inorg. Chim. Acta* **1985**, *15*, 96.
[25] J. P. Collman, C. T. Sears Jr., M. Kubota, *Inorg. Synth.* **1969**, *11*, 101.
[26] R. G. Goel, W. O. Ogini, *Organometallics* **1982**, *1*, 654.
[27] R. G. Goel, R. G. Montemayor, W. O. Ogini, *J. Am. Chem. Soc.* **1978**, *100*, 3629.
[28] D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.* **1980**, 1213.
[29] J. M. Clear, J. M. Kelly, C. M. O'Connell, J. G. Vos, C. J. Cardin, S. R. Costa, *J. Chem. Soc., Chem. Commun.* **1980**, 750.
[30] R. F. Jones, D. J. Cole-Hamilton, *Inorg. Chim. Acta* **1981**, L3.
[31] D. Choudury, R. F. Jones, G. Smith, D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.* **1982**, 1143.
[32] J. M. Kelly, C. M. O'Connell, J. G. Vos, *J. Chem. Soc., Dalton Trans.* **1986**, 253.
[33] B. P. Sullivan, D. J. Salmon, T. T. Meyer, *Inorg. Chem.* **1978**, *17*, 3334.
[34] R. J. Forster, A. Boyle, J. G. Vos, R. Haze, A. J. G. Dijkhuis, R. A. G. de Graeff, J. G. Haasnoot, R. Prins, J. Rudijk, *J. Chem. Soc., Dalton Trans.* **1990**, 121.
[35] I. R. Baird, S. J. Rettig, B. R. James, K. A. Skov, *Can. J. Chem.* **1998**, *76*, 1379.
[36] T. Tatsumi, H. Tominaga, M. Hidai, Y. Uchida, *J. Organomet. Chem.* **1981**, *215*, 67.
[37] M. J. Camenzind, B. R. James, D. Dolphin, J. W. Sparapany, J. A. Ibers, *Inorg. Chem.* **1988**, *27*, 3054.
[38] Ph. Serp, M. Hernandez, Ph. Kalck, *C. R. Acad. Sci. Paris* **1999**, 267.
[39] M. J. Clear, W. P. Griffith, *J. Chem. Soc. A* **1970**, 2788.
[40] R. Colton, R. H. Farthing, J. Knapp, *Aust. J. Chem.* **1970**, *23*, 1351.
[41] R. J. Judd, R. Cao, M. Bliner, T. Armbruster, H.-B. Bürgi, A. E. Merbach, A. Ludi, *Inorg. Chem.* **1995**, *34*, 5080.
[42] C. H. Cheng, D. E. Hendriken, R. Eisenberg, *J. Am. Chem. Soc.* **1977**, *99*, 2791.
[43] D. Forster, *Inorg. Nucl. Lett.* **1969**, *5*, 433.
[44] B. B. Wayland, R. F. Schramm, *Inorg. Chem.* **1969**, *8*, 971.

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