Preliminary communication

THE NOVEL FORMATION OF AN ACETONE ENOLATE COMPLEX VIA THE ADDITION OF METHYLLITHIUM TO THE ACYLRHODIUM(I) COMPOUND Rh(COMe)(CO)(triphos) (triphos = MeC(CH₂PPh₂)₃)

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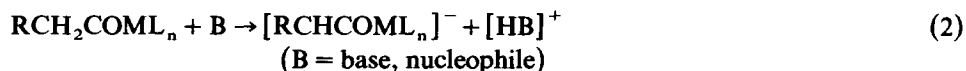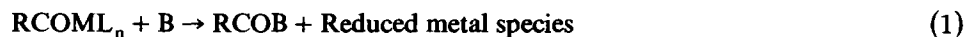
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Summary

The compound Rh(COMe)(CO)(triphos) appears to react with methyllithium via addition to the acetyl carbon atom to form the complex [Rh{C(O)Me$_2$}(CO)(triphos)]$^-$, rather than via the expected deprotonation of the acetyl group to form the enolate (ketene) complex [Rh(CH$_2$CO)(triphos)]$^-$.

Although nucleophilic addition to a wide variety of unsaturated organic ligands is a very common process in organotransition metal chemistry [1], reactions of acylmetal compounds with nucleophiles and bases seem limited to nucleophilic displacement of the acyl group [2] (eq. 1) and deprotonation of the acyl group [3] (eq. 2).

$$RCOML_n + B \rightarrow RCOB + \text{Reduced metal species} \tag{1}$$

$$RCH_2COML_n + B \rightarrow [RCHCOML_n]^- + [HB]^+ \tag{2}$$
$$(B = \text{base, nucleophile})$$

The anionic metal enolate species of eq. 2 have found considerable utility in the elaboration of acyl ligands, as they generally undergo electrophilic attack at carbon rather than oxygen [3a–d]. The complexes often also exhibit the properties expected of ketene complexes and, indeed, can eliminate the ketenes RCH=C=O [3e–f]. Reactions as in eq. 1 generally appear to involve attack by, for instance, alkoxide ion on the acyl carbon atom, resulting in the formation of esters [2], but such reactions appear to be rare. In general, deprotonation rather than nucleophilic addition occurs when acylmetal complexes are treated with strong bases/nucleophiles.

We now wish to report new examples of nucleophilic addition to an acylrhodium(I) complex. We have earlier reported and discussed aspects of the

chemistry of triphos-ruthenium complexes (triphos = the tridentate ligand MeC(CH$_2$PPh$_2$)$_3$), including oxidative additions of the ruthenium(0) complex Ru(CO)$_3$(triphos) [4] and resolution of chiral, octahedral ruthenium(II) complexes of the type [RuMe(CO)(L)(triphos)]X [5]. It was felt that analogous chemistry of rhodium(I) and rhodium(III) should prove equally interesting, and we have found that the readily prepared [Rh(CO)$_2$(triphos)]PF$_6$ (I) and RhCl(CO)(triphos) (II) [6,7] provide very convenient starting points. Both are susceptible to nucleophilic addition at carbon monoxide, I, for instance, reacting with a suspension of NaBH$_4$ in THF at $-60°$C to give a compound exhibiting a resonance in the ^{1}H NMR spectrum at $\sim \delta$ 12 ppm, presumably [8] the formyl compound Rh(CHO)(CO)(triphos) (III) (eq. 3).

$$[Rh(CO)_2(triphos)]^+ + H^- \rightarrow Rh(CHO)(CO)(triphos) \qquad (3)$$
$$\quad (I) \qquad\qquad\qquad\qquad (III)$$
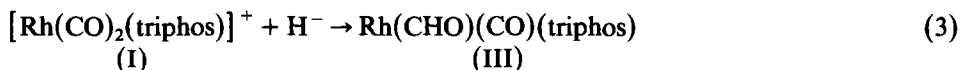
However, III is thermally unstable, and readily converts (eq. 4) at higher temperatures to the hydride complex RhH(CO)(triphos) (IV) (ν(CO) 1909 cm^{-1}; δ(H) -8.35 ppm, J(H–P) 33 Hz, J(H–Rh) 15 Hz), which has been prepared elsewhere [9] by a different route.

$$III \rightarrow RhH(CO)(triphos) \qquad\qquad\qquad\qquad (4)$$
$$\qquad (IV)$$

Compound I also reacts smoothly with methyllithium (1 equiv. in THF) to form the new acetyl compound Rh(COMe)(CO)(triphos) (V) (ν(CO) 1909 cm^{-1}, ν(C=O) 1635 cm^{-1}; δ(Me)(^{1}H) 2.14 ppm). Compound V is rather labile, however, and converts reversibly to the methyl compound RhMe(CO)(triphos) (VI) (ν(CO) 1901 cm^{-1}; δ(Me)(^{1}H) -0.14 ppm, J(H–P) 5.2 Hz, J(H–Rh) 1.5 Hz), which can also be prepared by treating II with methyllithium [10].

$$I + MeLi \rightarrow Rh(COMe)(CO)(triphos) \xrightarrow{-CO} RhMe(CO)(triphos) \qquad (5)$$
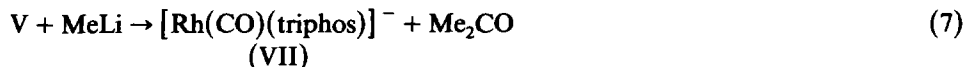$$\qquad\qquad\qquad (V) \qquad\qquad\qquad\qquad\qquad (VI)$$
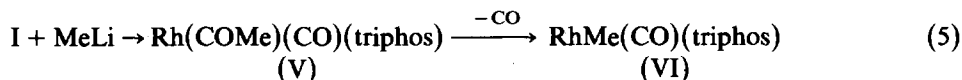
It was surprising, therefore, to find on several occasions that treatment of I with excess methyllithium and then ethanol (added to destroy unreacted methyllithium) yielded in several instances the hydride IV. In an attempt to ascertain the route by which IV was formed, the reaction of a THF solution of I with methyllithium under a nitrogen atmosphere at room temperature was monitored by ^{31}P{^{1}H} NMR spectroscopy.

As expected, addition of one equivalent of methyllithium to a solution of I (δ(P) 10.1 ppm, J(P–Rh) 98.6 Hz) resulted in the almost complete conversion of I to V (δ(P) 4.9 ppm, J(P–Rh) 110 Hz). Interestingly, addition of a second equivalent of methyllithium resulted in the formation of a mixture of IV and a new compound VII exhibiting a phosphorus resonance at δ 21.4 ppm (J(P–Rh) 155 Hz). Treatment of VII in turn with ethanol (a proton source), methyl iodide or acetyl chloride at room temperature resulted in the rapid appearance of the phosphorus resonances of IV, VI or V, respectively. Compound VII thus exhibits the chemical properties anticipated of the rhodium($-$I) complex [Rh(CO)(triphos)]$^-$, a conclusion supported by the observation of a carbonyl stretching mode in the IR spectrum of a

solution of VII at 1691 cm^{-1} [12], and by the fact that VII is generated (by ^{31}P{^{1}H} NMR spectroscopy) in THF by sodium amalgam reduction of I.

Further investigations of the products of reactions of I with excess methyllithium showed that t-butoxide ion (but not methane) and VII were the only products formed [14], and thus the sequence of steps would appear to be as in eq. 6–8.

$$I + MeLi \rightarrow Rh(COMe)(CO)(triphos) \qquad (6)$$
$$(V)$$

$$V + MeLi \rightarrow [Rh(CO)(triphos)]^- + Me_2CO \qquad (7)$$
$$(VII)$$

$$Me_2CO + MeLi \rightarrow Me_3CO^- \qquad (8)$$

While we have as yet no definitive information regarding the mechanisms of these reactions, the absence of methane during the formation of VII would appear to preclude enolate formation via deprotonation as in eq. 2. In addition, treatment of a solution of V with lithium diisopropylamide, a strong but bulky base, resulted in no reaction. It thus seems likely that the reaction of V with methyllithium involves addition to the acyl carbonyl carbon atom (presumably the most electrophilic site) to produce [Rh(COMe$_2$)(CO)(triphos)]$^-$ (VIII). However VIII cannot be the compound responsible for the phosphorus resonance at δ 21.4 ppm because protonation and methylation of VIII would be very unlikely to result in the direct formation of IV and VI, respectively. Instead, it seems likely that VIII spontaneously decomposes to VII and acetone, the latter in turn reacting with methyllithium to form the t-butoxide anion [15]. If, however, excess methyllithium is not present, VII is sufficiently basic that it can deprotonate the acetone to form IV.

We have also observed that IV does not react with acetone, but is deprotonated by methyllithium to form VII. However, the latter reaction is too slow at room temperature to be involved in the reactions described by eq. 6–8. The rhodium($-$I) species VII also reacts reversibly with carbon monoxide at room temperature to form a new species exhibiting phosphorus resonances at δ 24.6 (J(P–Rh) 157 Hz) and δ -26 (s) (ratio $\sim 2/1$). The upfield resonance has a chemical shift very close to that of free triphos, suggesting displacement of one of the phosphorus atoms by a carbonyl group. The new species exhibits ν(CO) at 1871 and 1814 cm^{-1}, and is probably the dicarbonyl rhodium($-$I) species [Rh(CO)$_2$(triphos)]$^-$, in which the triphos coordinates in a bidentate manner.

It is not clear why the acylrhodium(I) complex described here undergoes only nucleophilic attack, in contrast to compounds of the type CpFe(CO)L(COR) (L = CO, tertiary phosphine) [3] which are deprotonated by strong bases. Electronic factors would presumably influence both processes in the same way, as significant back donation from the metal, for instance, would both render the acyl-carbonyl carbon less electrophilic and lower the acidity of the acyl group protons.

References

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7 Both compounds are expected to assume trigonal bipyramidal structures with one axial and two equatorial phosphorus atoms [6], but they are fluxional in solution. The $^{31}P\{^1H\}$ spectrum of I in CD_2Cl_2 exhibits a doublet resonance (δ 10.1 ppm, J(Rh–P) 98.6 Hz) down to $-90°C$, that of II a doublet at δ 5.5 ppm (J(Rh–P) 105 Hz). The $^{31}P\{^1H\}$ MAS-NMR spectrum of solid I does exhibit the expected non-equivalent resonances.

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10 Compound VI has also been characterized by elemental analyses. Other alkylrhodium complexes of this type have been reported while this work was in progress [9,11].

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12 This value of ν(CO) is rather low compared with previous reports of supposedly similar anionic species [13], and may indicate the existence of a bridging carbonyl group. However, the previously reported anions were not well characterized [13].

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14 t-Butanol was detected by GC and by ^1H (δ(Me) 1.23 ppm) and $^{13}C\{^1H\}$ (δ(Me) 30.7 ppm, δ(C) 70.5 ppm) NMR spectroscopy following hydrolysis of the reaction mixture.

15 Alkoxide ions appear to be innocuous in the system under consideration. I and II react very slowly with sodium methoxide to give small amounts of IV, but no acyl species. Furthermore, there is no reaction between V and excess lithium methoxide.