Journal of Organometallic Chemistry, 142 (1977) C65—C68

Preliminary communication

A REACTIVE RHODIUM(I) CARBONYL DITHIOLATE AND THE FORMATION OF ACYL AND HYDRIDE SPECIES

CHIEN-HONG CHENG, DAN E. HENDRIKSEN, and R. EISENBERG*

Department of Chemistry, University of Rochester, Rochester, New York 14627 (U.S.A.)

(Received August 2nd, 1977)

Summary

The rhodium(I) complex $[Rh(CO)(PEt_3)(mnt)]^-$ (mnt = maleonitriledithiolate) reacts with a variety of alkyl halides to form acyl complexes isolated in the presence of excess PEt_3 as five-coordinate species of formula $[Rh(COR)(PEt_3)_2(mnt)]$. The structure of the complex for R = n-Pr has been determined by an X-ray analysis, and is found to be a square-based pyramid with the acyl group in the apical position. Addition of $HClO_4$ to the rhodium(I) anion in the presence of excess PEt_3 yields rhodium(III) hydride, $[RhH(CO)(PEt_3)_2(mnt)]$, while addition of acid to the rhodium(I) complex in CH_3CN solution with ethylene present leads slowly to formation of an acyl complex which is isolated as $[Rh(COEt)(PEt_3)_2(mnt)]$ upon phosphine addition. A novel alkyl group migration from the acyl carbon to a donor S atom is also observed in monophosphine systems.

The reaction of rhodium(I) complexes with alkyl halides is limited by both complex and substrate reactivity [1, 2]. Recently, we observed that chelation of rhodium(I) by the dianionic ligand maleonitriledithiolate (mnt) greatly increases the reactivity of this d^8 metal center [3], and herein we report the further enhancement of this reactivity through the use of PEt_3 as an ancillary ligand in the system. Moreover, while the bis-phosphineacyl complexes are found to be stable, square pyramidal species, the monophosphine systems show an unusual alkyl group migration from the acyl carbon atom to a sulfur donor ligand with concomitant reduction of rhodium(III) to rhodium(I).

The complex $[Rh(CO)(PEt_3)(mnt)]^-$ (A) is formed by the PEt_3 substitution of carbon monoxide from $[Rh(CO)_2(mnt)]^-$ [4]. Only one of the carbonyl ligands is displaced, as determined by an IR-monitored titration of the dicarbonyl complex with PEt_3 in CH_2Cl_2, and the monocarbonyl species A persists even with excess phosphine present. The values of $\nu(CO)$ for $[Rh(CO)_2(mnt)]^-$ are 1985 and 2035 cm^{-1} (KBr) while that for A is 1945 cm^{-1} in CH_2Cl_2*.

*The cations for A may be PPh_4^+, $AsPh_4^+$, $n\text{-}Bu_4N^+$, etc.

Complex A, which is generated in situ, reacts with a variety of alkyl halides RX (for X = I, R = Me, Et, n-Pr, n-Bu, n-$C_{10}H_{21}$; for X = Br, R = Et, n-Pr, n-Bu, benzyl, allyl; for X = Cl, R = allyl) to yield stable acyl complexes which are isolated in the presence of excess PEt_3 as analytically pure products of formula [Rh(COR)$(PEt_3)_2$(mnt)] (B). Complex A also reacts with i-PrI, albeit incompletely, to give the corresponding isobutyryl complex (methyl protons located at δ 0.73 ppm, the α-proton resonance is not found because of probable overlap with PEt_3 resonances). The incompleteness of the reaction was found by monitoring ν(CO) over time. The reactivity of A is thus significantly greater than its PPh_3 analog which reacts only with alkyl iodides and activated alkyl bromides [3], and it represents an extension over previously studied rhodium(I) complexes in their reactions with alkyl halides*.

The formation of B probably occurs via oxidative addition, alkyl migration to form an anionic acyl species and phosphine substitution of the halide ion. Direct evidence for the last step is observed when A is allowed to react with benzyl bromide in the absence of excess PEt_3. The α-methylene protons of the anionic phenylacetyl species [Rh($COCH_2Ph$)Br(PEt_3)(mnt)]$^-$ (C) exhibit an AB quartet at δ 4.12 ppm. indicating magnetic nonequivalence. Addition of PEt_3 results in rapid conversion of the AB quartet to a singlet at δ 3.57 ppm characteristic of the isolated product B. The diastereotopic nature of the α-methylene protons in PPh_3 complexes of type C has been observed previously by us [3], and the structure of these anionic complexes has been shown to be square pyramidal with the acyl group in the apical position.

To establish the structure of the neutral acyl complexes B, a single crystal X-ray analysis of [Rh(CO-n-Pr)$(PEt_3)_2$(mnt)] was performed. Crystal data: *Pbca*, *a* 20.47(4), *b* 13.61(3), *c* 18.44(4) Å, Z = 8, ρ_{obs} 1.40(2) g/cm^3, ρ_{calc} 1.42 g/cm^3. Intensity data were collected by the $\theta - 2\theta$ counter technique, and the structure was solved and refined by standard methods to R and R' of 0.040 and 0.059 for 2614 observations and 253 variables.

The structure of the neutral acyl complex is shown in Fig. 1. The coordination geometry is square pyramidal with the acyl group in the apical position. Although similar in structure to the anionic complex C, the presence of two PEt_3 ligands in the basal plane removes the chirality at the Rh center and renders the α-methylene protons equivalent. The Rh—C distance of 2.001(7) Å is relatively short for a Rh—C σ bond [5—7] and suggests the significance of the "metalloenolate" resonance form (Rh=C$\overset{}{-}$O$^-$) in a bonding description of the acylmetal unit.

The reactivity of A is further evinced by hydride formation when acids are added to a THF solution of the complex. With excess PEt_3 present, the addition of $HClO_4$ (70% aq.) yields an isolable yellow-orange hydride D whose ^{1}H NMR spectrum exhibits an upfield hydride resonance which appears as a doublet of triplets at δ −9.79 ppm (^1J(Rh—H) 15 Hz, ^2J(P—H) 11 Hz). Values of ν(CO) and ν(Rh—H) for D are 2045 and 2000 cm^{-1}, respectively. Based on these observations and elemental analyses, we identify D as [RhH(CO)$(PEt_3)_2$(mnt)] with an octahedral structure having either *cis*- or *trans*-phosphines. In both cases the phosphines are equivalent and *cis* to the hydride ligand.

* In these studies [1, 2] alkyl halides were limited to active ones such as MeI, $PhCH_2Br$, allyl bromide, etc.

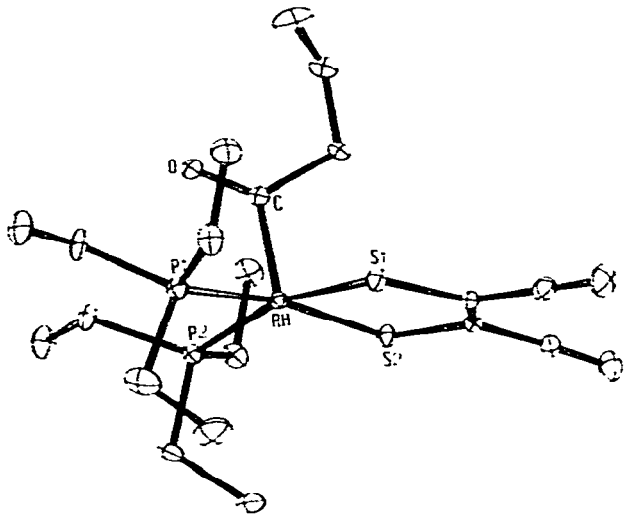

Fig. 1. A perspective drawing of [Rh(CO-n-Pr)(PEt_3)$_2$(mnt)]. Important bond parameters are: Rh—C, 2.001(7) Å; Rh—S, 2.311(5) and 2.328(4) Å; Rh—P, 2.344(5) and 2.349(5) Å; angle P—Rh—P, 96.83(8)°; and angle S—Rh—S, 87.19(10)°.

In the absence of excess PEt_3, the addition of *p*-toluenesulfonic acid or $HClO_4$ to yellow THF solutions of A yields an immediate red color which rapidly changes to brown, indicating complex decomposition. With ethylene present in CH_3CN, however, this same reaction followed by PEt_3 addition leads to the formation of an acyl complex which is shown by ^1H NMR and IR spectroscopy to be B with R = Et. This reaction thus corresponds to isolation of several of the established steps in hydroformylation catalysis [8], i.e., olefin coordination, insertion into a M—H bond, and R group migration to give a bound acyl.

One of the most intriguing aspects of the chemistry of these acylrhodium complexes containing the mnt ligand involves the controlled migration of the R group within the coordination sphere. For example, the reaction of [Rh(COEt)I-(PEt_3)(mnt)]$^-$ with Ag^+ in THF leads to an isolable neutral acyl complex* which, when dissolved and heated in CH_2Cl_2 or THF, transforms to the rhodium(I) S-alkylated complex [Rh(CO)(PEt_3)(Et-mnt)] (E)**. The migration appears to proceed via a sequence of 1,2-shifts from the acyl-carbon to rhodium and then to sulfur, and is completely suppressed in coordinating solvents and in the presence of free phosphine. This reaction, which is under investigation, suggests a possible means of maintaining an alkyl group proximate to a reactive d^8 metal center in metal complex-assisted syntheses.

---

*A pure sample of the neutral acyl complex could not be obtained due to the presence of a small amount of the corresponding S-alkylated compound. The neutral acyl complex exhibits ν(CO) bands at 1711s and 1766m cm^{-1}, and the NMR spectrum of the complex reveals the presence of THF even after extended drying in vacuo. In analogy with the isolated, analytically pure compounds [Rh(COR)(PPh_3)-(MeCN)(mnt)], the neutral acyl species is probably the five-coordinate system [Rh(COEt)(PEt_3)(THF)-(mnt)].

**The value of ν(CO) of E is 1993 cm^{-1} and the S-bound ethyl group shows proton resonances at δ 3.42 q and 1.46 t ppm. The structure of Rh(CO)(PPh_3)(Et-mnt), which has been determined and will be reported shortly [9] confirms the structure of E and the notion of alkyl group migration.

Acknowledgements

We wish to thank the National Science Foundation for support (Grant CHE 76-17440), Matthey Bishop, Inc. for a loan of rhodium salts, and Mr. C. Kubiak for help with the X-ray determination. C.-H.C. gratefully acknowledges an Elon Huntington Hooker Graduate Fellowship.

References

1 (a) I.C. Doueck and G. Wilkinson, J. Chem. Soc. (A) (1969) 2604; (b) A.J. Deeming and B.L. Shaw, ibid., (1969) 597; (c) M.C. Baird, J.T. Mague, J.A. Osborn and G. Wilkinson, ibid., (1967) 1347.
2 (a) A.J. Oliver and W.A.G. Graham, Inorg. Chem., 9 (1970) 243; (b) H.D. Empsall, E.M. Hyde, C.E. Jones and B.L. Shaw, J. Chem. Soc. Dalton, (1974) 1980; (c) R.F. Heck, J. Amer. Chem. Soc., 86 (1964) 2796; (d) D. Forster, ibid., 98 (1976) 846.
3 C.-H. Cheng, B.D. Spivack and R. Eisenberg, J. Amer. Chem. Soc., 99 (1977) 3003.
4 N.G. Connelly and J.A. McCleverty, J. Chem. Soc. A, (1970) 1621.
5 G.W. Adamson, J.J. Daly and D. Forster, J. Organometal. Chem., 71 (1974) C17.
6 P.G.H. Troughton and A.C. Skapski, Chem. Commun., (1968) 575; ibid., (1969) 666.
7 J.P. Collman, P.A. Christian, S. Current, P. Denisevich, T.R. Halbert, E.R. Schmittou and K.O. Hodgson, Inorg. Chem., 15 (1976) 223.
8 (a) C.K. Brown and G. Wilkinson, J. Chem. Soc. A, (1970) 2753; (b) G. Yagupsky, C.K. Brown and G. Wilkinson, ibid., (1970) 1392.
9 C.-H. Cheng and R. Eisenberg, manuscript in preparation.