

Chelated Dicarbene Complexes of Rhodium(III)

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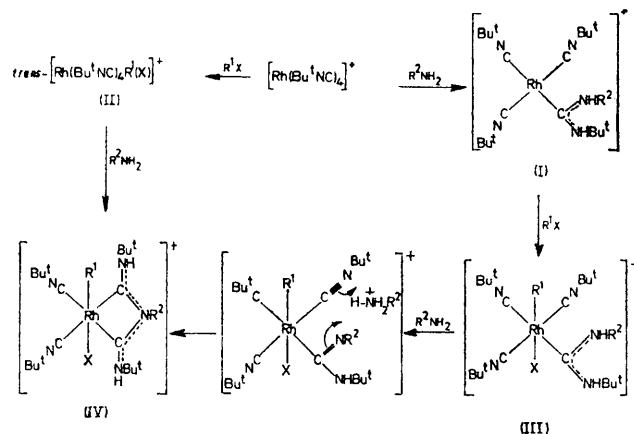
Summary Whereas, reaction of $[\text{Rh}(\text{Bu}^t\text{NC})_4]^+$ with primary amines affords diaminocarbene complexes, the reaction of $[\text{RhR}^1(\text{X})(\text{Bu}^t\text{NC})_4]^+$ ($\text{R}^1 = \text{alkyl}$, $\text{X} = \text{halogen or Bu}^t\text{NC}$) or $[\text{RhR}^1\text{C}(\text{NHR}^2)(\text{NHBu}^t)(\text{Bu}^t\text{NC})_3]^+$ with primary amine R^2NH_2 gives chelated dicarbene complexes.

RECENTLY^{1,2} it has been shown that the reaction (reflux, 12 h; MeOH) of $[\text{Fe}(\text{MeNC})_6]^{2+}$ with MeNH_2 affords the interesting chelated dicarbene complex $[\text{FeC}(\text{NHMe})\text{NMeC}(\text{NHMe})(\text{MeNC})_4]^{2+}$. On the basis of the observation that the ruthenium analogue forms only a monocarbene complex $[\text{Ru}\{\text{C}(\text{NHMe})_2\}(\text{MeNC})_5]^{2+}$, and that NH_3 reacts with $[\text{Fe}(\text{MeNC})_6]^{2+}$ to give $[\text{Fe}\{\text{C}(\text{NH}_2)\text{NHMe}\}(\text{MeNC})_5]^{2+}$ the

assumption was made that a monocarbene species is an intermediate in the formation of the chelated dicarbene complex. In a related study³ the cation $[\text{Os}(\text{MeNC})_6]^{2+}$ yielded a tris-monodentate carbene complex. However, the stepwise reaction path to the chelated dicarbene was not directly proved. In continuing our investigation⁴ of the reaction of rhodium(I) isocyanide complexes with amines we have firmly established a stepwise reaction path for the formation of chelated dicarbene rhodium(III) complexes.

Whereas, the reaction of amines (neat) with the cation $[\text{Rh}(\text{Bu}^t\text{NC})_4]^+$ results⁴ in nucleophilic attack upon only one co-ordinated isocyanide to yield the monodentate diaminocarbene complexes (I) $[\text{Rh}\{\text{C}(\text{NHR})(\text{NHBu}^t)\}(\text{Bu}^t\text{NC})_3]^+$ ($\text{R} = \text{Me, Et, Pr}^n, \text{Bu}^n$), the room-temperature reaction (minutes) of the Rh^{III} complexes (II) obtained by

the oxidative addition of R^1X to $[Rh(Bu^tNC)_4]^+$, with primary amines affords the chelated dicarbene complexes (IV) in high yield (Scheme). For example, treatment of $[RhMe(I)(Bu^tNC)_4]^+BF_4^-$ with $MeNH_2$ affords (IV; $R^1 = Me$, $X = I$, $R^2 = Me$) [m.p. 95° , ν (Nujol) 3280m (NH), 3200w (NH), 2205s (NC), 2185s (NC), and 1552s ($N\cdots C\cdots N$) cm^{-1} ; 1H n.m.r. resonances ($CDCl_3$) at τ 3.62br (s, 2H, $NHBu^t$), 6.90 (s, 3H, CH_3N), 8.37 (s, 18H, Bu^tN), 8.45



(s, 18H, Bu^tN), and 9.10 (d, 3H, CH_3Rh , J_{Rh-H} 2.0 Hz)]. The ^{13}C n.m.r. spectrum of the complex (IV; $R^1 = Me$, $R^2 = Bu^t$, $X = I$) obtained from the corresponding reaction with Bu^tNH_2 showed resonances ($CDCl_3$) at δ -7.1 ($Me-Rh$, J_{Rh-C} 20.0 Hz), 6.65-32.3 (Bu^t), 32.3, 29.0 and 29.1

† The ^{13}C n.m.r. spectrum of $[Rh(Bu^tNC)_4]^+$ shows resonances at δ 29.8 [$(CH_3)_3CNC$, J_{H-C} 131.0 \pm 3.0 Hz], 57.9 [$(CH_3)_3CNC$], and 130.7 [$(CH_3)_3CNC$, J_{Rh-C} 52.0 \pm 3.0 Hz, J_{N-C} 18.0 \pm 3.0 Hz]; and $[RhMe(I)(Bu^tNC)_4]^+$ at δ 29.6 [$(CH_3)_3CNC$, J_{H-C} 140.0 \pm 3.0 Hz], 59.8 [$(CH_3)_3CNC$], and 123 br [$(CH_3)_3CNC$, unresolved coupling]; and (III; $R^1 = Me$, $R^2 = Bu^t$, $X = I$) at δ 14.0-33.0 (Bu^t), 29.7 and 30.1 [each $(CH_3)_3CNC$], 54.0, 55.1, 59.5, and 59.8 [all $(CH_3)_3CNC$]. The carbene carbon and isocyanide Bu^tNC could not be unambiguously determined.

¹ J. S. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 1971, **93**, 4613.

² D. J. Doonan and A. L. Balch, *J. Amer. Chem. Soc.*, 1973, **95**, 4769.

³ J. Chatt, R. L. Richards, and G. H. D. Royston, *J.C.S. Dalton*, 1973, 1433.

⁴ P. R. Branson and M. Green, *J.C.S. Dalton*, 1972, 1303.

[each $(CH_3)_3CNC$], 49.5, 53.7, 58.6, and 59.0 [all $(CH_3)_3CNC$], and 154br [$(CH_3)_3CNC$], and 187.2(carbene C, J_{Rh-C} 35.0 Hz).† The addition of methylamine to the dication $[Rh-Me(Bu^tNC)_6]^{2+}$ also afforded directly the chelated dicarbene complex (IV; $R^1 = Me$, $R^2 = Me$, $X = Bu^tNC$).

Although the Rh^{III} monodentate diaminocarbene complexes (III) obtained by the oxidative addition of RX to (I) showed no evidence in a variety of solvents of cyclising to form the chelated dicarbene, the addition of, for example, *n*-propylamine to (III; $R^1 = Me$, $R^2 = Pr^t$, $X = I$) resulted in rapid reaction to give (IV; $R^1 = Me$, $R^2 = Pr^t$, $X = I$). Similar reactions occurred with other primary amines.

Thus, these experiments define a reaction path to the chelated dicarbene complexes *via* monocarbene complexes. In the base-prompted 'zipping up' reaction the added amine has a dual role, in removing a proton from the monocarbene or amidinium complex, and then transferring a proton to the adjacent co-ordinated isocyanide. Although it is certainly not possible to assess the relative importance of electronic and steric effects in this reaction, these observations underline the importance of a proximity effect, in that in (I) the plane of the carbene is almost certainly perpendicular to the metal plane, there being an appreciable barrier to rotation, whereas, in (III) the presence of the substituents R and X probably has the effect of forcing the carbene into the plane containing the rhodium and the three remaining isocyanides.

[(Received, 27th February 1974; Com. 247.)