Journal of Organometallic Chemistry, 57 (1973) C103–C106

Preliminary communication

Gold carbene complexes as intermediates in the α-addition of amines to isocyanides

JOHN E. PARKS and ALAN L. BALCH

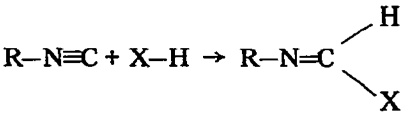
Department of Chemistry, University of California, Davis, California 95616 (U.S.A.)

(Received May 30th, 1973)

SUMMARY

The reaction of amines and isocyanides with tetrachloroaurate(III) yields carbene complexes of the type $Au\{C(NHR)NR'R''\}_2^+$. Under thermal decomposition or treatment with added ligands (cyanide ion or methyl isocyanide) the carbene ligands are liberated to yield formamidines.

The metal ion catalysed α-addition (eqn.1) of a variety of heteroatom-hydrogen bonds to isocyanides have been reported[1]. Despite the existence of numerous reports that stable carbene ligands are formed by the addition of amines, alcohols, or thiols to coordinated isocyanides[2,3] no direct evidence linking complexes containing these ligands to the α-addition reactions has been discovered since our initial suggestion[4] that such carbene complexes might be intermediates in this reaction.

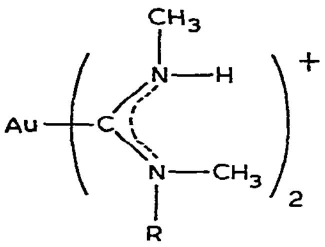


$$R{-}N{\equiv}C + X{-}H \rightarrow R{-}N{=}C\begin{matrix} \diagup H \\ \diagdown X \end{matrix} \qquad (1)$$

(X = N,P,O,S,Si)

Tetrachloroaurate has been shown to function as a catalyst in the α-addition of piperidine to cyclohexyl isocyanide[5]. The importance of gold carbene complexes in this reaction is now demonstrated by the isolation of such complexes from mixtures of tetrachloroaurate, isocyanide and amine, and in the subsequent generation of formamidine from these complexes.

Treatment of aqueous $AuCl_4^-$ with methyl isocyanide and methylamine yields the colorless cation I. An analogous reaction with dimethylamine produces II. Reaction of



(I) R = H

(II) R = CH$_3$

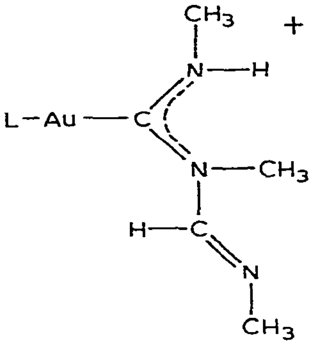
$AuCl_4^-$, cyclohexyl isocyanide and piperidine yields $Au[C(NHC_6H_{11})N(CH_2)_5]_2^+$ (III). In the absence of piperidine this latter reaction produces the colorless isocyanide complex $Au(CNC_6H_{11})_2^+$ (IV)*. All of these complexes have been isolated as their hexafluorophosphate salts and have been characterized by elemental analysis, conductivity, and by IR and PMR spectra. The infrared spectrum of I shows two bands at 3445 and 3395 cm^{-1} due to ν(NH) as well as absorptions at 2950 (ν(CH)), 1590 (δ(NCN)) and 1530 (δ(NH)) whereas II exhibits only a single ν(NH) at 3390 and other similar absorptions at 2945, 1585 and 1500. Consistent with their formulations I, II, and III do not exhibit infrared bands in the ν(C≡N) region whereas IV exhibits two ν(C≡N) bands (in a Polyfluor mull) at 2255 and 2245 cm^{-1} The PMR spectrum of I in dimethylsulfoxide-d_6 consists of two methyl doublets at τ6.76 (3) (J(H–N–C–H) 5.0 Hz) and 6.60 (3) (J(H–N–C–H) 4.5 Hz) and two poorly resolved NH quartets at 1.98 (1) and 1.57 (1). Due to the partial double bond character of the C–N bonds, the ligand is constrained to a planar geometry; the steric requirements of the methyl groups force it to assume the *amphi* configuration and cause non-equivalence of the methyl and N–H groups. The PMR spectrum of II which consists of a doublet at τ6.76 (3) (J(H–N–C–H) 4.5 Hz) due to the methyl group on the proton bearing nitrogen, singlets at 7.10 (3) and 6.49 (3) due to the other two methyl groups, and a broad resonance at 3.34 (1) due to the nitrogen bound proton, indicates similar electronic and steric constraints on the ligands of II.

Under a variety of conditions these complexes react to yield formamidines. Treatment of I or II with two equivalents of cyanide ion in dimethylsulfoxide solution at 25° results in the nearly quantitative release of *N,N'*-dimethylformamidine and *N,N,N'*-trimethylformamidine respectively. The conditions utilized for the release of the ligands from I and II by cyanide are the mildest yet found for the simple displacement of carbene ligands. The pattern of these reactions, which involve rearrangement of the freed ligand by transferring a proton from a position α to the carbene carbon to the carbene carbon, has also been observed in other cases where carbene ligands are displaced$^{6-8}$.

---

* The liberation of carbon dioxide upon the addition of methyl isocyanide to an aqueous solution of tetrachloroauric acid suggests that the reduction of Au^{III} to Au^{I} proceeds via coordination and subsequent oxidative hydrolysis of the isocyanide.

Methyl isocyanide also reacts with II to yield *N,N,N'*-trimethylformamidine. However this reaction occurs much more slowly than the displacement by cyanide ion. Whereas with cyanide the ligand displacement is complete upon mixing, with methyl isocyanide at least 8 hours are required to produce enough formamidine to be detected by PMR spectroscopy. Methyl isocyanide also reacts with I but in this case the product is the diamidide[9] $CH_3N{=}CHN(CH_3)CH{=}NCH_3$*. We believe that this product arises via the initial release of *N,N'*-dimethylformamidine which then attacks a coordinated isocyanide to yield the complex V (L is a neutral carbene or isocyanide ligand) which subsequently is attacked by another isocyanide ligand and releases the diamidide. In the solid state the gold carbene complexes undergo thermal decomposition above 120°. The volatile products of the decomposition of II consist of dimethylamine, methyl isocyanide, and *N,N,N'*-trimethylformamidine. This is the first indication that the addition of amine to isocyanide to give a carbene ligand may be reversed.



(V)

Saegusa *et al.* have noted that $AuCl_4^-$ is an efficient catalyst for the addition of *N*-methylaniline to cyclohexyl isocyanide at 160° but a rather poor catalyst for the addition of piperidine to this isocyanide at 17° [5]. The difference in catalytic activity may be understood in terms of the two steps of the catalytic process: addition of amine to coordinated isocyanide and displacement of the carbene ligand by isocyanide. At 17°, a gold carbene complex is formed with piperidine but is relatively stable to displacement, as we have shown, whereas a higher temperature (160°) is required both for addition of the weaker nucleophile, *N*-methylaniline and for the displacement of the resulting carbene ligand at a catalytically useful rate. Metals such as Cu^I which form less stable metal—carbon bonds than does Au^I are consequently better catalysts for the α-addition reaction at lower temperatures provided that they sufficiently activate the isocyanide toward the initial nucleophilic addition .

---

* This diamidide (which has been fully characterized) has been prepared independently by heating *N,N'*-dimethylformamidine above 100°.

ACKNOWLEDGEMENT

This research was supported by Grant GM 18357 from the National Institute of Health.

REFERENCES

1 T. Saegusa and Y. Ito, in I. Ugi, (Ed.), *Isonitrile Chemistry*, Academic Press, New York, 1971, p. 65.
2 F.A. Cotton and C.M. Lukehart, *Prog. Inorg. Chem.*, 16 (1972) 487.
3 D.S. Cardin, B. Cetinkaya and M.F. Lappert, *Chem. Rev.*, 72 (1972) 545.
4 A. Burke, A.L. Balch and J.E. Enemark, *J. Amer. Chem. Soc.*, 92 (1970) 2555.
5 T. Saegusa, Y. Ito, S. Kobayashi, K. Hirota and H. Yoshioka, *Bull. Chem. Soc. Jap.*, 42 (1969) 3310.
6 E.O. Fischer and A. Maasböl, *J. Organometal. Chem.*, 12 (1968) P15.
7 E.O. Fischer, *Rev. Pure Appl. Chem.*, 24 (1970) 407.
8 J.A. Connor and P.D. Rose, *J. Organometal. Chem.* 46 (1972) 329.
9 F.C. Cooper, M.W. Partridge and W.F. Short, *J. Chem. Soc.*, (1951) 391.