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GOLD CARBENE COMPLEXES: PREPARATION, OXIDATION, AND LIGAND DISPLACEMENT

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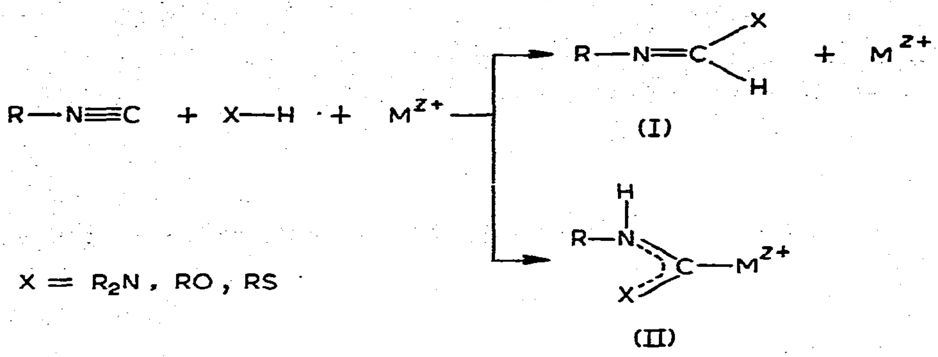
Summary

The reaction of isocyanides and amines with $AuCl_4^-$ produces bis(carbene) complexes of the type $Au\{C(NR_2)NR'H\}_2^+$. Treatment of $(C_6H_5)_3PAuCl$ with methyl isocyanide in basic methanol produces cyclic $[AuC(OCH_3)NCH_3]_3$ which is cleaved by hydrogen chloride to give $HNCH_3(CH_3O)CAuCl$. In the solid state these Au^I complexes luminesce under ultraviolet irradiation. Treatment of $Au\{C(NHCH_3)_2\}_2^+$, $Au\{C(NHCH_3)N(CH_3)_2\}_2^{2+}$ and $HNCH_3(CH_3O)CAuCl$ with cyanide ion in dimethyl sulfoxide solution produces $HC(NCH_3)NHCH_3$, $HC(NCH_3)N(CH_3)_2$ and $HC(OCH_3)NCH_3$, respectively. Other ligand displacement reactions are described. Methyl isocyanide reacts with $Au\{C(NHCH_3)_2\}_2^+$ to yield the diamidide $CH_3N{=}CHN(CH_3)CH{=}NCH_3$ which is also formed upon prolonged heating of *N,N'*-dimethylformamidine. These ligand displacement reactions establish the role of carbene complexes as intermediates in the α-addition reaction of protic nucleophiles with isocyanides.

Introduction

In the presence of metal ions, isocyanides will react with protic nucleophiles to yield two classes of products. On one hand a purely organic product, I, may result (the so-called α-addition reaction [1]), while in other cases stable metal carbene complexes, II, are formed [2]. Although the relationship between these two reactions has made it apparent that carbene complexes may be intermediates in the formation of I, most of the carbene complexes prepared from isocyanides are extremely robust and few efforts have been made to displace these carbene ligands from the metal.

Recently we have briefly reported the preparation of some carbene complexes of Au^I [3]. These complexes are unusual in that the carbene ligands may be readily displaced to give formamidine derivatives and consequently the intermediacy of the carbene complexes in the α-addition reaction has been established. This report concerns further characterization of these gold carbene complexes.



Several other reports of related gold carbene complexes derived from isocyanides have appeared [4—6].

Experimental

Methyl isocyanide [7] (toxic), *N,N'*-dimethylformamidine [8], *N,N,N'*-trimethylformamidine [9], and *N*-methylformiminomethyl ester [10] were prepared by standard methods.

Conductivities were determined by use of an Industrial Instruments conductivity bridge with ~10^{-3} *M* nitromethane solutions. Infrared spectra were obtained from fluorocarbon and Nujol mulls and recorded on a Beckman IR-12 spectrometer. Proton magnetic resonance (PMR) spectra were recorded on a Varian A-60 or JEOL JNM-MH-100 spectrometer. A Varian M66 double focussing mass spectrometer was utilized for determining mass spectra.

$[Au\{C(NHCH_3)_2\}_2][PF_6]$. Methyl isocyanide (0.50 ml, 9 mmol) was added to a solution of 0.50 g (1.3 mmol) of sodium tetrachloroaurate in 10 ml of water. After the initial yellow precipitate had dissolved, 2 ml (23 mmol) of 40% aqueous methylamine, was added to the yellow solution. Upon the addition of a saturated methanolic solution of ammonium hexafluorophosphate, the colorless product crystallized (yield 0.5 g, 80%). After collecting and washing with water, the product was purified by recrystallization from acetone/2-butanol; conductivity: Λ 101 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$. (Found: C, 14.85; H, 3.45; N, 11.45. $C_6H_{16}AuF_6N_4P$ calcd.: C, 14.82; H, 3.32; N, 11.52%.)

$[Au\{C(NHCH_3)N(CH_3)_2\}_2][PF_6]$. This colorless complex was prepared from aqueous dimethylamine using the procedure described for $[Au\{C(NHCH_3)_2\}_2][PF_6]$. (Found: C, 18.76; H, 3.78; N, 11.02. $C_8H_{20}AuF_6N_4P$ calcd.: C, 18.69; H, 3.92; N, 10.90%.)

$[Au\{C(NHCH_3)_2\}_2I_2][PF_6]$. A solution of 0.49 g (1.9 mmol) of iodine in 25 ml of dichloromethane was added to a solution of 0.94 g (1.9 mmol) of $[Au\{C(NHCH_3)_2\}_2][PF_6]$ in 35 ml of methanol. The solution was heated under reflux for 0.5 h. After the addition of 25 ml of 2-butanol, the volume of the solution was reduced on a rotary evaporator until crystals of the product formed. The yellow crystals (yield 1.3 g, 90%) were collected, washed with 2-butanol and vacuum dried: conductivity: Λ 93 $cm^2 \cdot mol^{-1} \cdot ohm^{-1}$. (Found: C, 9.97; H, 2.21; N, 7.75. $C_6H_{16}AuF_6I_2N_4P$ calcd.: C, 9.74; H, 2.18; N, 7.57%.)

$[HC(NHCH_3)N(CH_3)_2][PF_6]$. Concentrated hydrochloric acid (1.0 ml) was added to 1.0 g of *N,N,N'*-trimethylformamidine dissolved in 3 ml of water.

The cloudy solution was filtered, and to it was added a saturated aqueous solution of ammonium hexafluorophosphate. The fine colorless needles which precipitated were collected by filtration and vacuum dried. Purification was accomplished by recrystallization from 4 ml of water: conductivity, Λ 100 cm^2 · ohm^{-1} · mol^{-1}. (Found: C, 20.60; H, 4.85; N, 12.05. $C_4H_{11}F_6N_2P$ calcd.: C, 20.69; H, 4.77; N, 12.06%.)

$CH_3N\{CH(NCH_3)\}_2$. Five grams of *N,N'*-dimethylformamidine were heated under reflux for 8 h during which time methylamine was evolved. The resulting liquid was distilled through a 12" spinning band column at 10 mm of Hg. The fraction distilling at 55-56° was collected and shown by PMR to contain 80% $CH_3N\{CH(NCH_3)\}_2$ and 20% starting material. A portion of this fraction was purified by gas chromatography at 130° on a 5' by 1/4" carbowax column to give ~100 μl of the pure product as a colorless liquid. (Found, C, 52.64; H, 9.66; mol. wt., 113. $C_5H_{11}N_3$ calcd.: C, 53.07; H, 9.80; mol. wt., 113.)

$[AuC(OCH_3)NCH_3]_3$. A solution of 0.15 g (2.7 mmol) of potassium hydroxide dissolved in 15 ml of methanol was added to a slurry of 1.38 g (2.8 mmol) of triphenylphosphine gold(I) chloride in 20 ml of methanol. The dropwise addition of 0.20 ml (3.0 mmol) of methyl isocyanide to this slurry caused the solid to dissolve, but precipitation of another colorless solid rapidly followed. After the mixture was stirred for 1 h, the solid was collected by filtration and washed with ether. Purification was accomplished by recrystallization from chloroform—methanol; m.p. 112-113°, yield 0.35 g (47%). The compound is a non-electrolyte in dichloromethane. (Found: C, 13.28; H, 2.23; N, 5.25. C_3H_6AuNO calcd.: C, 13.39; H, 2.25; N, 5.21%.)

$[ClAuC(OCH_3)NHCH_3]$. Hydrogen chloride was briefly bubbled through a slurry of 0.23 g (0.85 mmol) of $[AuC(OCH_3)NCH_3]_3$ in 2 ml of chloroform until all of the solid dissolved. After filtration, addition of ether to the solution yielded the complex as colorless crystals (yield 0.16 g, 62%). The product was recrystallized from chloroform—ether. (Found: C, 11.37; H, 2.23; Cl, 11.22; N, 4.31. $C_3H_7AuClNO$ calcd.: C, 11.79; H, 2.31; Cl, 11.60; N, 4.58%.)

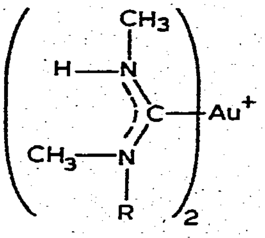
$[Au(CNC_6H_{11})_2][PF_6]$. Cyclohexyl isocyanide (0.4 ml, 4 mmol) was added to a solution of 0.4 g (1 mmol) of sodium tetrachloroaurate in 10 ml of water. Enough methanol was added to dissolve the yellow precipitate. Addition of a saturated methanol solution of ammonium hexafluorophosphate caused the precipitation of a mixture of yellow and white needles. The yellow needles are presumed to be $Au(CNC_6H_{11})_nPF_6$ (n = 3 or 4) and are only stable in the presence of a large excess of cyclohexyl isocyanide. Recrystallization of the dried precipitate from 1-propanol served to purify the white crystalline product: conductivity, Λ 100 cm^2 · ohm^{-1} · mol^{-1}. (Found: C, 30.12; H, 4.15; N, 5.41. $C_{14}H_{22}AuF_6N_2P$ calcd.: C, 30.01; H, 3.96; N, 5.00%.)

$[Au\{C(NHC_6H_{11})N(CH_2)_5\}_2][PF_6]$. Cyclohexyl isocyanide (0.5 ml, 5 mmol) and piperidine (1.0 ml, 10 mmol) were added to a solution of 0.45 g (1.1 mmol) of sodium tetrachloroaurate in 15 ml of water and 15 ml of methanol. A saturated, aqueous solution of ammonium hexafluorophosphate was added to precipitate the colorless product. After collecting and drying, the solid product was purified by dissolution in 3 ml of acetone followed by filtration and the gradual addition of ether (yield 1.0 g): conductivity, Λ 100 cm^2 · ohm^{-1} · mol^{-1}. (Found: C, 40.54; H, 6.20; N, 8.30. $C_{24}H_{44}AuF_6N_4P$ calcd.: C, 39.45; H, 6.07; N, 7.67%.)

Ligand displacement reactions. The reaction of tetraphenylarsonium cyanide with $Au\{C(NHCH_3)_2\}_2PF_6$ offers a typical example. A solution of 42 mg (1 mmol) of the complex was prepared in 0.5 ml of dimethylsulfoxide-d_6 and to this was added 2.5 mmol of tetraphenylarsonium cyanide. The PMR spectrum of the solution indicated that none of the starting complex remained after 5 min. Instead the only components detected by PMR were tetraphenylarsonium ion and *N,N'*-dimethylformamidine; the latter was identified by comparison with an authentic sample. Further verification of the identity of the formamidine was obtained by adding two drops of trifluoroacetic acid to the sample. After the addition the spectrum of *N,N'*-dimethylformamidinium ion was observed.

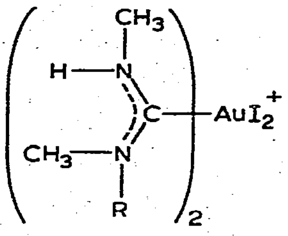
Results

The addition of methylamine and methyl isocyanide (in any order) to an aqueous solution of tetrachloroaurate(III) produces the colorless cation III which has been isolated as the air stable hexafluorophosphate salt. A similar reaction employing dimethylamine produces IV. Treatment of these Au^I complexes with a mole of iodine results in oxidation of the metal to produce the Au^{III} complexes V and VI. Conductivity measurements indicate that these salts are 1/1 electrolytes in nitromethane solution. The infrared and PMR spectral data for these and other new compounds are recorded in Tables 1 and 2. These spectra are analogous to those reported for similar carbene complexes [11, 12] and are consistent with carbene ligands which are constrained to a planar geometry with restricted rotation about the C—N bonds.



(III) R = H

(IV) R = CH3



(V) R = H

(VI) R = CH3

The reduction of Au^{III} to Au^I that is involved in the preparation of III and IV appears to proceed via coordination and subsequent hydrolysis of isocyanide. Addition of methyl isocyanide to an aqueous solution of tetrachloroauric acid results in the liberation of carbon dioxide. We have not achieved separation of the mixture of gold complexes that results from this reaction. However, the colorless cation $Au(CNC_6H_{11})_2^+$ has been isolated after treatment of tetrachloroaurate(III) with cyclohexyl isocyanide. Other examples of the reduction of Au^{III} by isocyanide have been reported [13]. Recrystallization of $Au(CNC_6H_{11})_2PF_6$ in the presence of excess cyclohexyl isocyanide produces unstable yellow needles which are probably $Au(CNC_6H_{11})_nPF_6$ (n = 3 or 4). However, these readily revert back into colorless $Au(CNC_6H_{11})_2PF_6$ and con-

TABLE 1

INFRARED DATA (cm^{-1})

Compound	ν(N—H)	ν(C—H)	ν(N═C═N),	δ(N—H)
$[Au\{C(NHCH_3)_2\}_2][PF_6]$	3455 s	2950 m	1595 vs	1528 w
	3395 s			
$[Au\{C(NHCH_3)N(CH_3)_2\}_2][PF_6]$	3400 s	2945 w	1588 vs	1515 w
$[Au\{C(NHCH_3)_2\}_2I_2][PF_6]$	3415 s	2945 w	1601 s	1545 w
	3340 s			
$[Au\{C(NHCH_3)N(CH_3)_2\}_2I_2][PF_6]$	3385 m	2930 m	1606 s	1580 sh
		2850 m		
$[HC(NHCH_3)N(CH_3)_2][PF_6]$	3398 s	2950 w	1730	1520
$[Au\{C(NHC_6H_{11})N(CH_2)_5\}_2][PF_6]$	3350 m	2930 s	1550 s	
		2845 m		
$[Au\{CNC_6H_{11}\}_2][PF_6]$		2930 s	2255 s[a]	
		2850 m	2245 s[a]	
$ClAuC(OCH_3)NHCH_3$	3280 vs	3050 w	1590 s	1510 w
		2990 w		
		2940 m		
		2850 m		
$[AuC(OCH_3)NCH_3]_3$		2982 w	1569	
		2925 m	1557 sh	
		2871 w		
		2826 m		

[a] ν(C≡N—)

TABLE 2

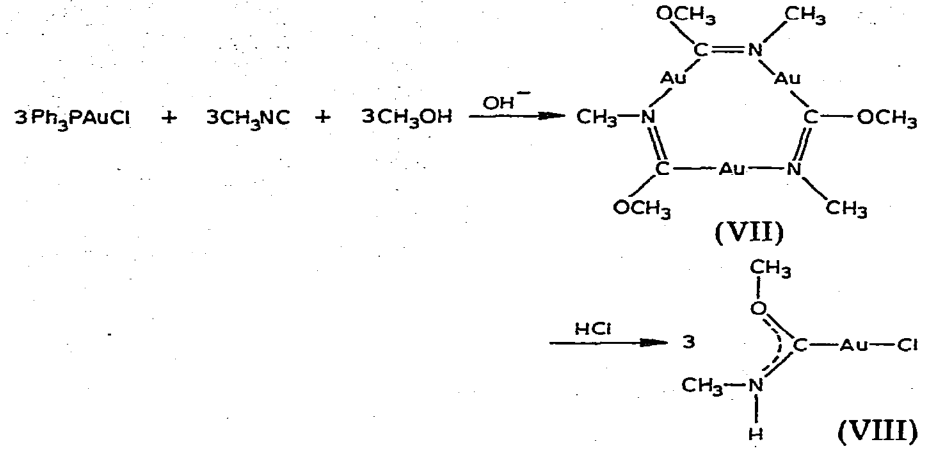
PMR DATA FROM DIMETHYL SULFOXIDE-d_6 SOLUTIONS

Complex	CH_3N	HN	HC
$[Au\{C(NHCH_3)_2\}_2][PF_6]$	7.28 (3,5.0 Hz)[a]	1.76(1)	
	6.88 (3,5.0 Hz)	1.97(1)	
$[Au\{C(NHCH_3)N(CH_3)_2\}_2][PF_6]$	7.16(3)		
	6.89 (3,4.5 Hz)	2.25(1)	
	6.63(3)		
$[Au\{C(NHCH_3)_2\}_2I_2][PF_6]$[b]	7.06 (3,5.2 Hz)	2.66(1)	
	6.90 (3,4.6 Hz)	2.90(1)	
$[Au\{C(NHCH_3)N(CH_3)_2\}_2I_2][PF_6]$	7.06 (3,4.4 Hz)	1.80(1)	
	6.99(3)		
	6.81(3)		
$[AuC(OCH_3)NCH_3]_3$[c]	6.88(3)		
	5.80(3)[d]		
$ClAuC(OCH_3)NHCH_3$	7.27 (3,5.0 Hz)	−0.23(1)	
	5.84(3)[d]		
$HC(NCH_3)NHCH_3$	7.23(6)	4.32(1)	2.76(1)
$[HC(NHCH_3)_2][CF_3CO_2]$	7.15 (3,5.1 Hz)	0.37(1)	2.02(1)[e]
	6.94 (3,4.3 Hz)	0.76(1)	
$HC(NCH_3)N(CH_3)_2$	7.32(6)		
	7.08 (3,1.3 Hz)[f]		3.70 (1,1.3 Hz)[f]
$[HC(NHCH_3)N(CH_3)_2][CF_3CO_2]$	7.03(3)		2.00(1)
	6.99 (3,4.4 Hz)	1.19(1)	
	6.84(3)		
$CH_3N(CHNCH_3)_2$	7.02(3)		
	6.94 (6,1.6 Hz)[f]		2.12 (2,1.6 Hz)[f]
$HC(OCH_3)NCH_3$	7.01 (3,1.4 Hz)[f]		1.48 (1,1.4 Hz)[f]
	5.65(3)[d]		
$[HC(OCH_3)NHCH_3][CF_3CO_2]$	7.56 (3,6.4 Hz)	2.4(1)	1.77(1)
	6.35(3)		

[a] Chemical shift, τ (relative intensity, coupling constant J(H—N—C—H). The HN and NCH_3 resonances which are coupled are given on the same horizontal line. [b] In acetonitrile-d_3. [c] In chloroform-*d*. [d] OCH_3 resonance. [e] J(H—C=N—H) 13.6, 6.0 Hz. [f] J(H—C=N—CH_3).

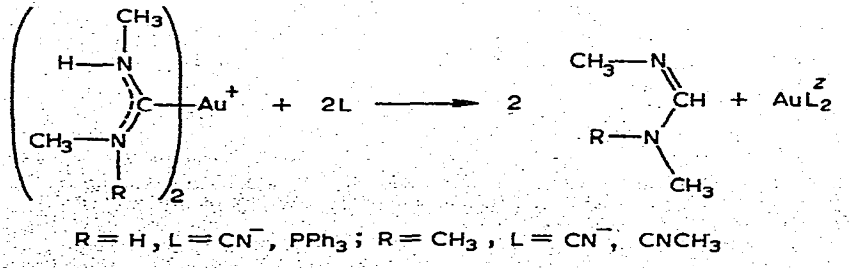
sequently complete characterization has not been possible. Treatment of tetrachloroaurate(III) with cyclohexyl isocyanide and piperidine yields the carbene complex $\mathrm{Au[C(NHC_6H_{11})N(CH_2)_5]_2^+}$ which is analogous to the formation of III and IV.

Treatment of triphenylphosphinegold(I) chloride with methyl isocyanide and base in methanol produces the complex VII which is formulated as a cyclic trimer by analogy with a number of other similar species [4]. Treatment of VII with hydrogen chloride results in cleavage of the trimer to produce the neutral carbene complex VII (eqn. 1).



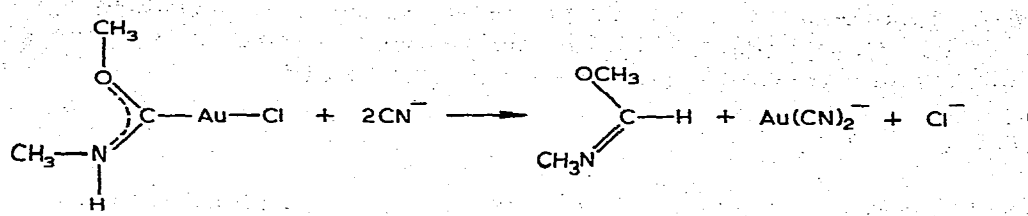
(1)

Upon addition of certain ligands the carbene ligands are readily displaced from the complexes III, IV and VIII (eqns. 2 and 3). Treatment of III or IV with two moles of cyanide ion in dimethyl sulfoxide solution results in the essentially quantitative formation of *N,N'*-dimethylformamidine or *N,N,N'*-trimethylformamidine respectively. Similarly, treatment of VIII with cyanide yields *N*-methylformiminomethyl ester, $\mathrm{HC(OCH_3)NCH_3}$. Triphenylphosphine also reacts with III to yield *N,N'*-dimethylformamidine. However, this reaction requires several hours to reach completion at room temperature whereas the displacement from III with cyanide ion is essentially complete after five minutes. In the presence of other potential ligands, pyridine, triphenylarsine, *N,N'*-dimethylformamidine, complex III remains unchanged for several days. It also should be noted that the solvent, dimethyl sulfoxide, which is also a potential ligand, does not show any evidence of a reaction with III over a one week period. Addition of cyanide to V also produces *N,N'*-dimethylformamidine. During the addition of cyanide ion, a series of color changes occurs and it is possible that reduction as well as ligand displacement occur during this process.



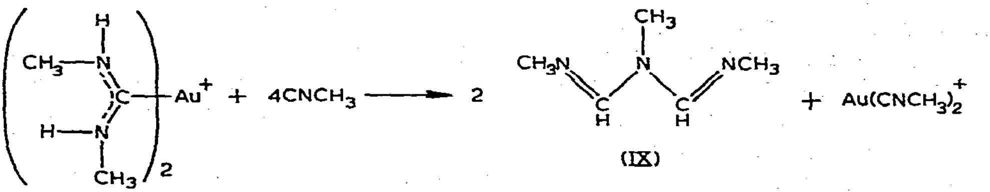
R = H, L = CN⁻, PPh3; R = CH3, L = CN⁻, CNCH3

(2)



(3)

In dimethyl sulfoxide solution, methyl isocyanide very slowly effects the displacement of the carbene ligands from III and IV. In the case of complex IV the product is *N,N,N'*-trimethylformamidine as expected. However, in the case of III the sole organic product that is detected is the diamidide IX (eqn. 4). This diamidide has also been prepared independently.



(IX)

(4)

Heating *N,N'*-dimethylformamidine at temperatures above 100°C for extended periods liberates methylamine and IX is formed. The new compound IX has been identified by elemental analysis and by its mass and PMR spectra. At least one other example of the condensation of two amidines to form a diamidide has been reported [14] although more commonly the thermolysis of amidines produces s-triazenes [15]. However, in the case of *N,N*-dimethylformamidine, the pattern of substitution precludes condensation to form an s-triazene.

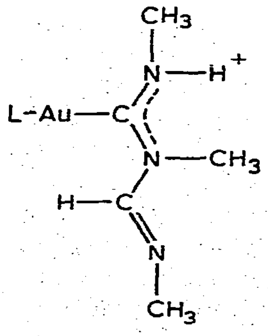
In the solid state the complexes III and IV undergo thermal decomposition above 120°. This appears to be a complicated process: some gold metal is produced so that redox processes as well as ligand displacement reactions occur. During the decomposition the solid phase experiences a decrease in weight which corresponds to approximately the loss of one ligand per mole of complex. The volatile products obtained from the decomposition of IV consist of dimethylamine, methyl isocyanide and *N,N,N'*-trimethylformamidine. The formation of methyl isocyanide and dimethylamine in this reaction must occur directly from the complex. Heating of *N,N,N'*-trimethylformamidinium hexafluorophosphate under these conditions does not produce any amine or isocyanide. Consequently, under drastic conditions the addition of amine to isocyanide may be reversed.

In the solid state these complexes possess another unusual property: under ultraviolet irradiation they exhibit intense luminescence. This property has been of use in ascertaining the purity and homogeneity of samples of these complexes. Although all of the complexes are white under normal illumination, they show some variety in the color and lifetime of their luminescence. The following is a list of the compounds which luminesce and the color observed: III, blue white; VII, orange; VIII, pink; $Au(CNC_6H_{11})_2PF_6$, blue white; $Au[C(NHC_6H_{11})N(CH_2)_5]_2PF_6$, white. In the case of VII the luminescence persisted for minutes after the ultraviolet irradiation was discontinued, in all other cases the luminescence ceased when the irradiation ceased. The Au^{III} complexes V and VI did not exhibit this phenomenon, nor did the related platinium and palladium complexes, $M\{C(NHCH_3)_2\}_4(PF_6)_2$ [11]. The luminescence of some other Au^I complexes containing triphenylphosphine has been reported [16].

Discussion

The bis(carbene) complexes of Au^I may be compared with the tetrakis(carbene) complexes of Pd^{II} and Pt^{II} [11]. These complexes and the bis(carbene) complexes of Hg^{II} [17] represent the only examples of metal ions coordinated solely by carbene ligands. The bis(carbene) complexes of Au^I are notably more reactive than the Pd^{II} and Pt^{II} tetrakis(carbene) complexes. This of course is due to both electronic and steric differences with the steric factors probably the major cause of the lower reactivity of the Pd^{II} and Pt^{II} complexes. The Au^I complexes undergo facile oxidation with iodine to yield Au^{III} complexes. Although other, less hindered Pt^{II} carbene complexes undergo oxidative additions [18, 19], $Pt\{C(NHCH_3)_2\}_4^{2+}$ is not oxidized by halogens probably because the planar carbene ligands are arranged to block the axial sites from further coordination. Similarly, the Au^I carbene complexes undergo facile ligand displacement in the presence of added ligands, but under similar or more extreme conditions the Pd^{II} and Pt^{II} tetrakis(carbene) complexes do not lose or exchange their ligands [11]. No studies of carbene ligand displacement from other less sterically encumbered Pd^{II} or Pt^{II} carbene complexes are available for comparison. In all probability the loss of formamidines from III and IV in the presence of additional ligands occurs by an associative mechanism as has been established for other Au^I complexes [20, 21]. The observation that the rate of ligand displacement is strongly dependent on the nature of the added ligand supports this idea.

The formation of the diamidide IX from the reaction of III with methyl isocyanide requires combination of one of the ligands of III, in either free or complexed form, with methyl isocyanide. There is no free *N,N'*-dimethylformamidine detected during the reaction. Consequently, we propose that methyl isocyanide adds to the cation III and then the $C_3H_7N_2$ moiety, in some form, attacks the coordinated isocyanide to form the unit X before the $C_3H_8N_2$ unit becomes completely free of the complex. Subsequent addition of another iso-

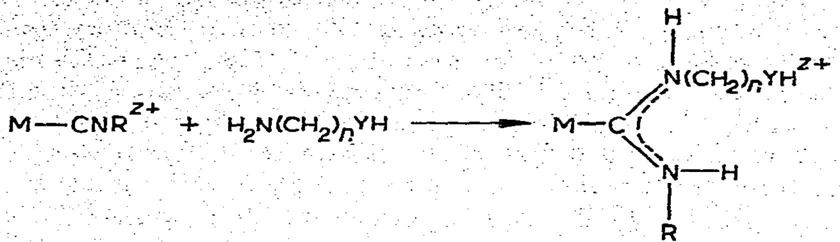

(X)

cyanide ligand allows release of the diamidide. An alternate mechanism for the formation of IX from the reaction of methyl isocyanide with III involves the initial release of *N*,*N*′-dimethylformamidine which then subsequently condenses with itself to expell methylamine and form IX. This mechanism appears unreasonable since not only is no free *N*,*N*′-dimethylformamidine observed during the reaction, but, in addition, the self condensation of *N*,*N*′-dimethylformamidine is much too slow to account for the formation of IX in this reaction.

The general pattern of reaction in the ligand displacement reactions involves transfer of hydrogen from a position α to the metal bound carbon onto that carbon after heterolytic cleavage of the metal—carbon bond. This pattern of behaviour has been observed for other types of metal carbene complexes when an α-hydrogen is present [22, 23]. The formation of *N*,*N*,*N*′-trimethylformamidine from the reaction of IV and methyl isocyanide as well as the isolation of $Au[C(NHC_6H_{11})N(CH_2)_5]^+$ from the reaction of tetrachloroaurate(III) with cyclohexyl isocyanide and piperidine indicates that metal carbene complexes are competent intermediates in the α-addition reactions of secondary amines to isocyanides. The observation that *N*,*N*′-dimethylformamidine and *N*-methylformiminomethyl ester are formed by ligand displacement from III and VIII respectively suggests that carbene complexes may also be intermediates in the α-addition of primary amines and alcohols to isocyanides. The reaction of III with methyl isocyanide, which produces the diamidide IX, presents a different reaction pattern. No other diamidide has been reported to result from the metal catalysed α-addition of primary amines to isocyanides and the generality of diamidide formation remains unexplored. It may be expected that the products resulting from the α-addition of primary amines with isocyanides will depend on the metal catalyst involved, the ligand (isocyanide or amine) which displaces the carbene ligand, and on the specific properties of the amine and isocyanide themselves. The only other examples involving gold catalysis of the α-addition reaction have employed secondary amines (piperidine and *N*-methylaniline) [24]. With other metals it is possible that an amine rather than an isocyanide adds to the metal center before the carbene ligand is lost and consequently the efficient formation of a diamidide would be precluded.

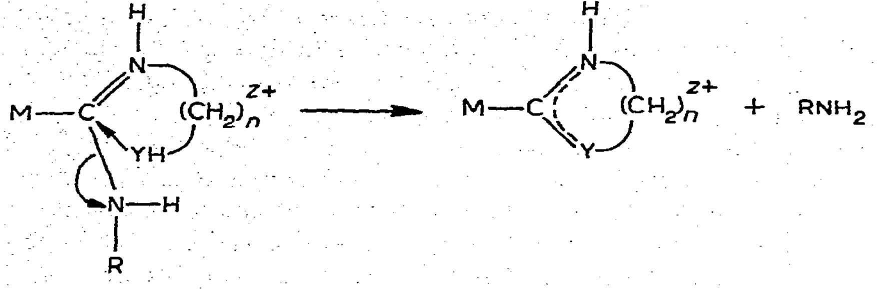
Although gold salts have been shown to act as catalysts in the α-addition reaction, other metals, especially Cu^I are better catalysts for this reaction. We have previously commented on the specific catalytic behavior of gold in this reaction [3] and we emphasize here that it is probably Au^I that is acting as the catalytic center since the Au^{III} initially introduced into the reaction is rapidly reduced to Au^I. In general in order to serve as a catalyst, the metal ion must be able to meet two requirements. It must be able to withdraw electrons from the donor carbon of the isocyanide in order to render that carbon more susceptible to nucleophilic attack. Such electron withdrawal generally manifests itself in an increase in the isocyanide stretching frequency in the coordinated form relative to the unbound form. An empirical correlation [25] suggests that this increase in isocyanide stretching frequency must exceed 40 cm^{-1} for an isocyanide ligand to be susceptible to nucleophilic attack by amines and alcohols. In agreement with this, coordination of cyclohexyl isocyanide to both Cu^I and Au^I produces significant increases in the isocyanide stretching frequency upon coordination (free $C_6H_{11}NC$, ν(CN) 2140 [24]; $Cu(CNC_6H_{11})Cl$, ν(CN) 2192 [24]; and

$Au(CNC_6H_{11})_2^+$, $\nu(CN)$ 2250 cm^{-1}). Secondly the metal must be able to release the carbene ligand once it is formed. As a result of this requirement metals like copper, which form relatively weak metal—carbon bonds, are more effective catalysts than gold or platinum.

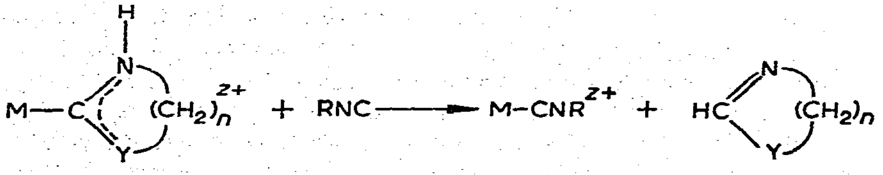


(5)

Y = NH, S, or O



(6)



(7)

Recently, the α-addition reaction has been extended to encompass the synthesis of various heterocycles [26]. We propose that this occurs via reactions 5—7. The additional feature required for this reaction is step 2 in which cyclization occurs through nucleophilic attack of Y upon the metal bound carbon atom. This carbon is of course electron poor and analogous reactions of amidinium ions, which these carbene ligands strongly resemble in their structure and reactivity, are known [27]. All of the other steps in the formation of these heterocycles are similar to those encoutered in the normal α-addition reaction.

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