Cationic Transition-metal Complexes. Part VI.[1] The synthesis of Dicarbene Complexes of Rhodium(III) and Iron(II)

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Treatment of $[\mathrm{RhR(CNBu^t)_4I}][\mathrm{BF_4}]$ (R = Me or Et) with neat $\mathrm{R'NH_2}$ (R′ = Me, $\mathrm{Pr^n}$, or $\mathrm{Bu^n}$) leads to the formation of the chelated dicarbene complexes $[\overline{\mathrm{Rh\{C(NHBu^t)NRC}}\mathrm{(NHBu^t)\}R(CNBu^t)_2I}][\mathrm{BF_4}]$. An alternative route to the dicarbene complex where R = Me and R′ = $\mathrm{Pr^n}$ is reaction of $[\mathrm{Rh\{C(NHPr^n)(NHBu^t)\}Me(CNBu^t)_3I}][\mathrm{BF_4}]$ with neat propylamine. Reaction of $[\mathrm{RhMe(CNBu^t)_4I}]^+$ with neat hydrazine affords a related dicarbene complex analogous to the Chugaveff salts. The use of neat amine as solvent in these reactions is extended to the synthesis of related 2,2′-bipyridyl and 1,10-phenanthroline iron(II) dicarbene complexes. The nature of the bonding and the mechanism of formation of these species is discussed.

THE chemistry of planar tetrakis(isocyanide)rhodium(I) complexes is characterised by oxidative-addition reactions which result in the formation of six-co-ordinate rhodium(III) isocyanide complexes.[2,3] The observation that the $[\mathrm{Rh(CNBu^t)_4}]^+$ cation[2] readily forms monocarbene adducts on reaction with amines, and that $[\mathrm{Fe(CNMe)_6}]^{2+}$ forms the chelating dicarbene complex[4] $[\overline{\mathrm{Fe\{C(NHMe)NMeC}}\mathrm{(NHMe)\}(CNMe)_4}]^{2+}$, suggested that the stereochemistry and mechanism of formation of these chelating dicarbene complexes could be studied in detail. A preliminary account of our work has been published,[5] which is further substantiated by studies on some iron(II) isocyanide species also described herein. In the course of the preparation of this manuscript a partially complementary study of the iron complexes was published.[6]

RESULTS

Although it has been shown that the cation $[\mathrm{Rh(CNBu^t)_4}]^+$ reacts with neat amines to afford[2] the monocarbene complexes (I), there was no evidence in these reactions for the formation of chelating dicarbene complexes of the type discovered by Balch and his co-workers in their study of the iron(II) system. However, the rhodium(III) species (II),[2] formed by *trans*-oxidative addition of alkyl iodides to $[\mathrm{Rh(CNBu^t)_4}]^+$, readily reacted at room temperature with neat primary amines to afford the chelating rhodium(III) dicarbene complexes (III)—(V). The availability of an alternative reaction path to these species *via* monocarbene complexes was demonstrated by the observation that treatment of complex (VI), obtained by oxidative addition of MeI to (I), with neat $\mathrm{Pr^nNH_2}$, afforded (III; R = $\mathrm{Pr^n}$) identical to that obtained directly from (II).

The i.r. and n.m.r. spectra of the dicarbene complexes is consistent with the illustrated structures. The i.r. spectrum showed NH stretches in the region 3 200—3 180 $\mathrm{cm^{-1}}$, in addition to two equally intense bands in the range 2 289—2 185 $\mathrm{cm^{-1}}$ assigned to ν(CN) of *cis*-isocyanide ligands and a strong absorption in the range 1 552–1 545 $\mathrm{cm^{-1}}$, assigned to the $\mathrm{N{\cdots}C{\cdots}N}$ moiety. The observed shift in ν(NC) in these complexes to lower wavenumber (*ca.* 40 $\mathrm{cm^{-1}}$) with respect to (II) is consistent with an increase in π back-bonding from the rhodium to the isocyanide antibonding (π^*) orbitals, and indicates that the chelating dicarbene ligand is a weaker π acceptor than the two isocyanide ligands from which it is derived.

In agreement with the illustrated structures, the ^{1}H n.m.r. spectra of the chelated dicarbene complexes showed a broad resonance at τ 2—4 assigned to the N*H* protons and resonances corresponding to the alkyl group R′ which, in the case of the methyl-substituted complexes, appeared as a singlet, there being no evidence (double irradiation) for coupling of the order of 5—7 Hz which would be expected if the arrangement MeNH was present. In addition, two $\mathrm{Bu^tN}$ singlet resonances of equal intensity (18 H) were observed, indicating the illustrated symmetrical structure; the low-field resonance is tentatively assigned to the co-ordinated $\mathrm{Bu^tNC}$ ligands, and the high-field resonance to the dicarbene system. These data do not exclude a symmetrical structure with the $\mathrm{Bu^tN}$ and N*H* hydrogen of the dicarbene system interchanged; however, examination of molecular models and also consideration of the mechanism (see later) for ring closure leads us to favour the illustrated structure. As expected, the ^{1}H n.m.r. spectra of all the complexes

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[1] Part V, M. Green and G. Parker, *J.C.S. Dalton*, 1974, 333.

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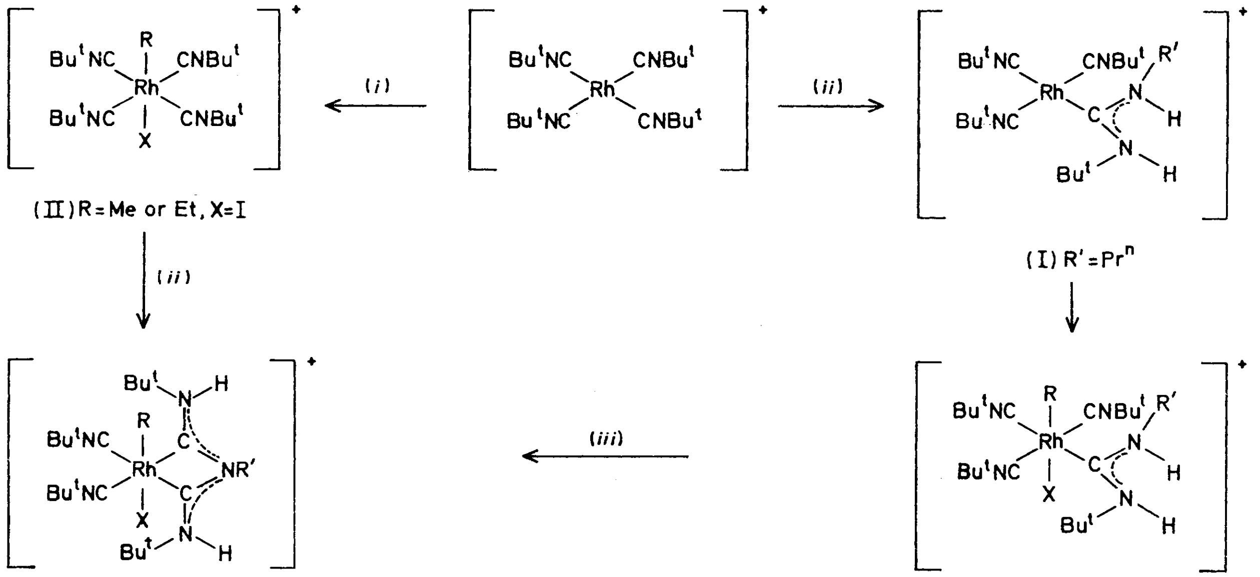
[3] J. W. Dart, M. K. Lloyd, R. Mason and J. A. McCleverty, *J.C.S. Dalton*, 1973, 2039.

[4] J. S. Miller, A. L. Balch, and J. A. Enemark, *J. Amer. Chem. Soc.*, 1971, **93**, 4613.

[5] P. R. Branson, R. A. Cable, M. Green, and M. K. Lloyd, *J.C.S. Chem. Comm.*, 1974, 364.

[6] D. J. Donnan and A. L. Balch, *Inorg. Chem.*, 1974, **13**, 921.



(II) R = Me or Et, X = I

(I) R′ = Prⁿ

(III) R = Me, R′ = Me, Prⁿ, cr Buⁿ, X = I
(IV) R = Et, R′ = Prⁿ or Buⁿ, X = I
(V) R = R′ = Me, X = BuᵗNC

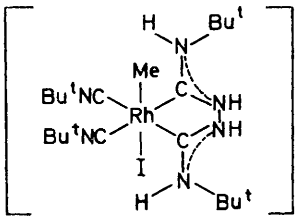
(VI) R = Me, R′ = Prⁿ, X = I

SCHEME 1 (*i*), RX; (*ii*), $R'NH_2$; (*iii*), Pr^nNH_2

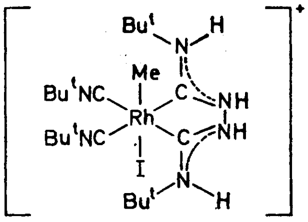
showed a high-field resonance corresponding to R–Rh, the signals showing appropriate $^1H-^{103}Rh$ coupling.

The ^{13}C Fourier-transform n.m.r. spectrum of (III; R = Bu^n) showed signals consistent with the postulated structure, and a chemical shift of 187 p.p.m. [$J(^{103}Rh-^{13}C)$ 35.0 Hz] was observed [5] for the carbene carbon atoms, the shift being compatible with that found for Balch's dicarbene complex * and other 1,3-substituted imidazolin-2-ylidene carbene complexes.[7]

That the formation of chelated dicarbene complexes is not restricted to halogenorhodium(III) species was shown by the fact that treatment of the dication $[RhMe(CNBu^t)_5]^{2+}$, obtained on addition of Bu^tNC to the five-co-ordinate species $[RhMe(CNBu^t)_4]^{2+}$, with neat methylamine led to rapid formation of complex (V), which showed the expected spectroscopic features.

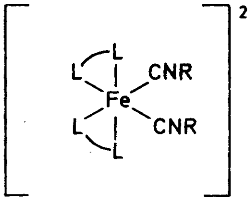


(VIIa)



(VIIb)

The relation of these reactions to the formation of the Chugaveff salts [8] is illustrated by the observation that when (II; R = Me) was dissolved in anhydrous hydrazine the 1 : 1 adduct (VII) was formed (0.5 h) as air-stable pale yellow crystals. The i.r. spectrum of (VII) showed bands characteristic of N*H*, terminal-bonded *cis*-isocyanide ligands, and a N$\cdots$C$\cdots$N system. However, although the ^1H n.m.r. spectrum showed resonances compatible with the illustrated structure, the available data do not allow a distinction to be made between structures (VIIa) and (VIIb). Since the former stereochemistry has been established by *X*-ray crystallography in the related complexes of Pd, Pt, and Fe, this orientation is preferred.



(VIII) L–L = 2,2′-bipyridyl, R = Me, Prⁱ, Buᵗ, or C_6H_{11}
(IX) L–L = 1,10-phenanthroline, R = Me, Prⁱ, Buᵗ, or C_6H_{11}

In all these reactions use of the reacting amine or hydrazine as the solvent was necessary for the formation of dicarbene complexes. It was, therefore, important to establish whether a similar solvent requirement was important in the related reactions of iron(II) isocyanide complexes. The iron(II) complexes $[Fe(CNR)_2(L-L)_2]^{2+}$, (VIII) and (IX) (L–L = 2,2′-bipyridyl or 1,10-phenathroline; R = Me, Pr^i, Bu^t, or C_6H_{11}), were readily obtained by reaction of $[Fe(L-L)_3]^{2+}$ with excess of isocyanide in acetone as solvent. The orange-red crystalline products were characterised by two strong absorptions (*cis* stereochemistry [9]) in

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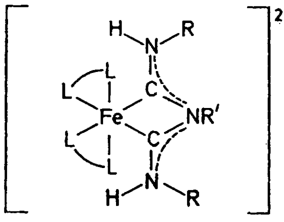
* The species $[\overline{Fe\{C(NHMe)NMeC}(NHMe)\}(CNMe)_4]^{2+}$ showed ^{13}C n.m.r. shifts (CD_3CN) of 28.9 (*Me*N), 34.4 (*Me*NH), 38.9 (*Me*NC), and 210.5 p.p.m. (carbenoid carbons).

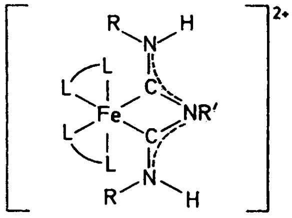
[7] D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, E. Randall, and E. Rosenburg, *J.C.S. Dalton*, 1973, 1982.

[8] G. Rouchias and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 2097.

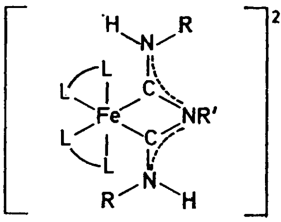
[9] R. E. De Simone and R. S. Drago, *Inorg. Chem.*, 1969, **8**, 2517; E. D. McKenzie, *Co-ordination Chem. Rev.*, 1971, **6**, 187.



(a)



(b)



(c)

(X) L-L = 2,2'-bipyridyl, R = R' = Me
(XI) L-L = 2,2'-bipyridyl, R = Pr^i, R' = Me
(XII) L-L = 1,10-phenanthroline, R = Pr^i, R' = Me

TABLE 1

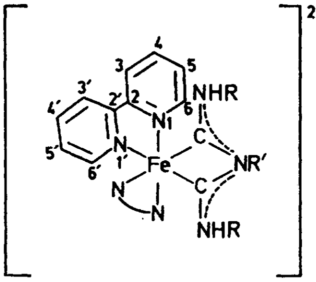
Data for the complexes $[Fe(L-L)_2(CNR)_2][PF_6]_2$ [L-L = bipy (VIII) or phen (IX)]

Complex	M.p. (θ_c/°C)	Analysis [a] (%) C	H	N	Λ [b] S cm^2 mol^{-1}	M-L Charge-transfer band ($10^{-3}\bar{\nu}$/cm^{-1}) [c]
(VIII; R = Me)	220 [d]	38.8 (38.9)	3.3 (3.0)	11.3 (11.4)	201	23.5 (3.64)
(VIII; R = Pr^i)	210	42.4 (42.2)	4.2 (3.8)	10.6 (10.6)	206	23.7 (4.09)
(VIII; R = Bu^t)	190	43.8 (43.7)	4.5 (4.1)	10.0 (10.2)	214	23.7 (4.06)
(VIII; R = C_6H_{11})	195	46.5 (46.6)	4.5 (4.3)	9.6 (9.6)	196	23.5 (4.08)
(IX; R = Me)	167	44.7 (42.6)	2.9 (2.8)	10.8 (10.7)	197	23.5 (3.63) 25.7 (3.66)
(IX; R = Me)	180	45.1 (45.5)	3.7 (3.6)	9.8 (10.0)	207	23.8 (3.77) 26.0 (3.80)
(IX; R = Pr^i)	160	46.6 (46.8)	4.3 (3.9)	9.2 (9.6)	190	23.8 (3.76) 26.0 (3.78)
(IX; R = Bu^t)	190	49.6 (49.4)	4.5 (4.1)	9.1 (9.1)	217	23.7 (3.77)
(IX; R = C_6H_{11})						25.8 (3.20)

[a] Calculated values are given in parentheses. [b] Measured in $MeNO_2$ using a Phillips conductivity meter; Λ = 180 S cm^2 mol^{-1} for a 2 : 1 electrolyte. [c] Electronic spectra were measured in CH_2Cl_2 on a Carey spectrophotometer; log ε values are given in parentheses. [d] None of the complexes melted below 325 °C, but transitions occurred at the recorded temperatures.

TABLE 2

^1H n.m.r.[a] and i.r.[b] data (cm^{-1}) for the complexes $[Fe(CNR)_2(bipy)_2]$ $[PF_6]_2$, (VIII), and (X) and (XI)



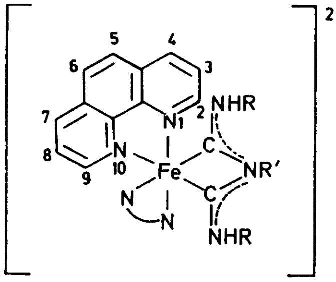
(X) R = R' = Me
(XI) R = Pr^i, R' = Me

Complex	ν(NC)	$H^{3,3'}$	$H^{4,4'}$	$H^{5,5'}$	$H^{6,6'}$	RN and RNH
(VIII; R = Me) [c]	2 215, 2 198	1.35	1.78	1.78, 2.58	0.70, 2.20	6.36 (s, 6 H, *Me*N)
(VIII; R = Pr^i)	2 190, 2 170	1.37	1.76	1.76, 2.34	0.81, 2.18	8.65 [t, 12 H, $CH\mathit{Me}_2$, *J* (HH) 7.0] 5.72 (m, 2 H, $C\mathit{H}Me_2$)
(VIII; R = Bu^t)	2 180, 2 160	1.29	1.72	1.72, 2.49	0.80, 2.12	8.56 (s, 18 H, B*u*^{t}N)
(VIII; R = C_6H_{11})	2 183, 2 165	1.32	1.75	1.75, 2.50	0.77, 2.18	7.80 (m), 8.26 (m), 8.76 (m)
(X) [d]		1.30	1.70	1.94, 2.56	1.00, 2.24	6.60 (sbr, 2 H, N*H*Me) 7.18 (s, 6 H, N*Me*) 7.44 (s, 3 H, N*Me*)
(XI) [e]		1.28	1.68	1.92, 2.50	0.98, 2.18	6.54 (s, 3 H, N*Me*) 7.60 (m, 4 H, $C\mathit{H}Me_2$ + N*H*) 8.93 [d, 6 H, $CH\mathit{Me}_2$, *J* (HH) 6.0] 9.33 [d, 6 H, $CH\mathit{Me}_2$, *J* (HH) 6.5]

[a] Chemical shifts (τ) were measured in $(CD_3)_2CO$; coupling constants, *J*, are in Hz. [b] Measured as a KBr disc. [c] ^{13}C N.m.r. shifts (in CD_3CN) at 31.5 (*Me*NC), 124.2 (C^5), 124.3 ($C^{5'}$), 127.9 (C^2), 128.4 ($C^{2'}$), 140.0 (C^3 and $C^{3'}$), 151.0 (C^6), 157.0 (C^2), 157.7 ($C^{6'}$), and 158.3 p.p.m. ($C^{2'}$). [d] ^{13}C N.m.r. shifts (in CD_3CN) at 29.6 (*Me*N), 32.2 (*Me*NH), 124.0 (C^5), 124.2 ($C^{5'}$), 127.0 (C^3), 128.6 ($C^{3'}$), 137.7 (C^4), 139.1 ($C^{4'}$), 151.8 (C^6), 156.4 ($C^{6'}$), 157.8 (C^2), 159 6 ($C^{2'}$), and 223.3 p.p.m. (carbenoid carbon). [e] ^{13}C N.m.r. shifts (in CD_3CN) at 22.7 ($NCHMe_2$), 23.9 ($NCHMe_2$), 29.1 (*Me*N), 50.7 ($NCHMe_2$), 123.9 (C^5), 124.0 ($C^{5'}$), 127.4 (C^3), 128.9 ($C^{3'}$), 138.0 (C^4), 138.3 ($C^{4'}$), 158.0 (C^2 and C^6), and 159.8 p.p.m. ($C^{2'}$ and $C^{6'}$)

TABLE 3

^{1}H n.m.r.[a] and i.r.[b] data (cm^{-1}) for the complexes [Fe(CNR)$_2$(phen)$_2$][PF$_6$]$_2$, (IX), and (XII)



(XII) R=Pr^i,R′=Me

Complex	ν(NC)	H^2	H^3	H^4	H^5	H^6	H^7	H^8	H^9	RN and RNH
(XVI)	2 210, 2 195	0.40	1.68	0.95	1.56	1.65	1.30	2.31	2.31	6.55 (s, 6 H, *Me*N)
(XVII)	2 190, 2 165	0.40	1.70	1.00	1.56	1.65	1.30	2.30	2.30	8.72 [t, 12 H, CHMe$_2$, *J* (HH) 6.8]
(XVIII)	2 180, 2 160	0.31	1.70	0.90	1.56	1.60	1.30	2.31	2.31	8.62 (s, 18 H, *Bu*^{t}N)
(XIX)	2 190, 2 170	0.40	1.70	1.00	1.56	1.65	1.30	2.31	2.31	7.74 (m), 8.30 (m), 8.80 (m)
(XXII)		0.52	1.70	1.10	1.70	1.70	1.70	2.31	2.31	4.5 (m, 4 H, C*H*, N*H*) 7.2 (s, 3 H, N*Me*) 8.90 [t, 12 H, CH*Me*$_2$, *J* (HH) 6.8]

[a] Chemical shifts (τ) were measured in (CD$_3$)$_2$CO; coupling constants, *J*, are in Hz. [b] Measured as a KBr disc.

the i.r. spectrum in the range 2 180—2 240 cm^{-1} (Table 1). Surprisingly, attempts to prepare analogous complexes with the aryl isocyanides *p*-MeC$_6$H$_4$NC and *p*-ClC$_6$H$_4$NC were unsuccessful even under forcing conditions.

Treatment of the complexes (VIII; R = Me and Pr^i) and (IX; R = Pr^i) with methylamine using the amine as solvent led to formation of the dicarbene complexes (X)—(XII), there being no evidence for the formation of intermediate monocarbene species. Interestingly, the reaction of (VIII; R = Bu^t) with methylamine afforded [Fe(bipy)$_3$]$^{2+}$ and an unidentified water-soluble crystalline material. The i.r. spectra of (X)—(XII) (Table 2) exhibited an absorption at 3 300 cm^{-1} assigned as an *NH* stretch, and a strong absorption at 1 550 cm^{-1}, assigned to the $N\overset{\cdots}{-}C\overset{\cdots}{-}N$ moiety; no absorptions in the region 2 000—2 400 cm^{-1} were found. The appearance of the doublets in the ^{1}H n.m.r. spectrum of (XI) (Table 2), assignable to the methyl groups of the Pr^i unit, indicates clearly that the adduct has either structure (XIa) or (XIb), the alternative structure (XIc) being excluded. The ^{13}C Fourier-transform n.m.r. data (Table 2) for these chelating dicarbene species, including [Fe{C(NHMe)NMeC(NHMe)}-(CNMe)$_4$]$^{2+}$, indicate that the carbene carbon atoms appear downfield from the isocyanide *C*NR carbons. These data, in conjunction with those obtained by Cardin *et al.*,[7] suggest that the shift of the carbene carbon bonded to two nitrogen atoms (175—220 p.p.m.) may well be structurally diagnostic. The suggestion that this is dependent on the *trans* influence also receives support from these data. The asymmetry of (XI) is clearly exhibited by the appearance of 10 distinct ^{13}C absorptions (Table 2) for the bipy ligand, and a doublet for the Pr^i methyl groups.

DISCUSSION

The results with the rhodium(III) system demonstrate that there is a reaction path to chelated dicarbene complexes *via* monocarbene complexes, and it is likely that a similar reaction sequence is involved in the formation of the iron(II) dicarbene complexes. There are three factors which could control the cyclisation reaction. A steric or proximity effect is implied in the failure of (I) or palladium(II) monocarbene complexes to undergo cyclisation. The carbene ligand in the four-co-ordinate square planar species is perpendicular to the plane of the other ligands and, as there is a barrier to rotation about the metal–carbene-carbon bond, the monocarbene ligand is prevented from achieving the required stereochemistry for attack on the other co-ordinated isocyanide ligands. A second contributing factor in (I) may be that in this low-valent species the other isocyanide ligands are involved in greater π back-bonding with the rhodium(I) metal atom, thereby rendering themselves less susceptible to nucleophilic attack. Similarly, the formation of monocarbene complexes [Fe{C(NHMe)(NH$_2$)}(CNMe)$_5$]$^{2+}$,[6] [Ru{C-(NHMe)$_2$}(CNMe)$_5$]$^{2+}$,[6] and [Os{C(NHMe)$_2$}$_3$(CNMe)$_3$]$^{2+}$ [10] has been attributed to the amino-substituted carbene ligand being less sterically demanding, and that the greater radius of ruthenium and osmium decreases the proximity of the co-ordinated ligands.

These results, however, take no account of the possible influence of the solvent. Whereas Donnan and Balch[6] were unable to achieve dicarbene complex formation with methylamine and (IX; R = Pr^i), the use of methylamine as solvent and reactant resulted in a rapid reaction at room temperature and formation of the chelated complex (XII).

Thus, provided that the co-ordinated isocyanide *cis* to the monocarbene ligand is sufficiently susceptible to nucleophilic attack, and secondly that the stereochemical requirements are satisfied,* the amine probably acts as a proton-transfer agent leading to cyclisation. It is hoped that kinetic measurements will confirm a second-order dependence on amine concentration.

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* In the octahedral rhodium(III) species and in the iron(II) system, it would be expected to be easier for the M–C(NHR)$_2$ system to adopt the correct stereochemistry for cyclisation.

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

EXPERIMENTAL

The ^{1}H n.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 MHz; chemical shifts are relative to tetramethylsilane (τ 10.00). ^{13}C Fourier-transform n.m.r. spectra were obtained on a Jeol JNM-PFT-100 spectrometer at 25.15 MHz with a deuterium internal lock; the chemical shifts are relative to tetramethylsilane. The i.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer using Nujol mulls. The complexes $[\mathrm{RhMe(CNBu^t)_4I}][\mathrm{BF_4}]$, $[\mathrm{RhEt(CNBu^t)_4I}][\mathrm{BF_4}]$, $[\mathrm{RhMe(CNBu^t)_4}][\mathrm{BF_4}]$, $[\mathrm{Fe(bipy)_3}]^{2+}$, $[\mathrm{Fe(phen)_3}]^{2+}$, $[\mathrm{Fe(bipy)(CN)_2}]$, and $[\mathrm{Fe(phen)_2(CN)_2}]$ were prepared by the published methods.[2,11]

Reactions of Iodo(methyl)tetrakis(t-butyl isocyanide)rhodium Tetrafluoroborate, (II; R = Me).—(a) *With methylamine.* An excess of anhydrous methylamine (5 cm^3) was condensed (−196 °C) into a Carius tube containing (II; R = Me) (0.20 g, 0.3 mmol). After 45 min at room temperature the tube was opened, and the excess of amine removed *in vacuo*. Recrystallisation of the residue from methylene chloride–diethyl ether afforded pale yellow crystals of *iodo(methyl)-[2-methyl-1,3-bis(t-butylamino)-2-azapropanediylidene]bis(t-butyl isocyanide)rhodium*(III) *tetrafluoroborate,* (III; R′ = Me) (0.14 g, 67%), m.p. 95 °C (decomp.) (Found: C, 38.2; H, 6.4; N, 10.1. $\mathrm{C_{22}H_{44}BF_4IN_5Rh}$ requires C, 38.0; H, 6.4; N, 10.0%), 3 280 m (NH), 3 200 w (NH), 2 205 s (NC), 2 185 s (NC), and 1 552 s ($\mathrm{N\cdots C\cdots N}$) cm^{-1}. The ^{1}H n.m.r. spectrum (in $\mathrm{CDCl_3}$) showed resonances at τ 3.62 (sbr, 2 H, $\mathrm{N}H\mathrm{Bu^t}$), 6.90 (s, 3 H, NMe), 8.37 (s, 18 H, $\mathrm{NBu^t}$), 8.45 (s, 18 H, $\mathrm{NBu^t}$), and 9.10 (d, 3 H, Rh*Me*, *J*(RhH) 2.0 Hz].

(b) *With propylamine.* A suspension of (II; R = Me) (0.20 g, 0.3 mmol) in propylamine (5 cm^3) was stirred at room temperature for 45 min to give a clear yellow solution. The excess of amine was removed *in vacuo* and the product recrystallised from methylene chloride–diethyl ether as yellow *crystals* of (III; R′ = $\mathrm{Pr^n}$) (0.15 g, 69%), m.p. 138 °C (decomp.) (Found: C, 39.4; H, 6.4; N, 9.7. $\mathrm{C_{24}H_{48}BF_4IN_5Rh}$ requires C, 39.9; H, 6.6; N, 9.7%), 3 290m (NH), 3 190w (NH), 2 209s (NC), 2 193s (NC), and 1 545s cm^{-1} ($\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}$). The ^{1}H n.m.r. spectrum (in $\mathrm{CDCl_3}$) showed resonances at τ 3.70 (sbr, 2 H, $\mathrm{N}H\mathrm{Bu^t}$), 6.21 [t, 2 H, $\mathrm{N}CH_2$, *J*(HH) 6.0 Hz], 8.37 (s, 18 H, $\mathrm{N}Bu^t$), 8.38 (m, 2 H, $\mathrm{NCH_2CH_2}$, identified by double irradiation), 8.45 (s, 18 H, $\mathrm{NBu^t}$), 9.00 [t, 3 H, $\mathrm{NCH_2CH_2CH_3}$, *J*(HH) 6.0 Hz], and 9.11 [d, 3 H, Rh*Me*, *J*(RhH) 2.0 Hz].

(c) *With butylamine.* In a similar reaction (1 h), complex (II; R = Me)(0.20 g, 0.3 mmol) and butylamine (5 cm^3) gave, after recrystallisation from methylene chloride–diethyl ether, pale yellow *crystals* of (III; R′ = $\mathrm{Bu^n}$)(0.15 g, 68%), m.p. 110—112 °C (decomp.) (Found: C, 40.5; H, 6.9; N, 9.5. $\mathrm{C_{25}H_{50}BF_4IN_5Rh}$ requires C, 40.7; H, 6.8; N, 9.5%), 3 285m (NH), 3 190w (NH), 2 207s (NC), 2 185s (NC), and 1 547s cm^{-1} ($\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}$). The ^{1}H n.m.r. spectrum (in $\mathrm{CDCl_3}$) showed resonances at τ 3.68 (sbr, 2 H, $\mathrm{N}H\mathrm{Bu^t}$), 6.18 [t, 2 H, $\mathrm{N}CH_2$, *J*(HH) 6.0 Hz], 8.3—8.5 (complex m, 4 H, $\mathrm{NCH_2}CH_2CH_2$), 8.38 (s, 18 H, $\mathrm{NBu^t}$), 8.45 (s, 18 H, $\mathrm{NBu^t}$), 9.10 [t, 3 H, $\mathrm{CH_2}CH_3$, *J*(HH) 6.0 Hz], and 9.15 [d, 3 H, Rh*Me*, *J*(RhH) 2.0 Hz].

Reactions of Iodo(ethyl)tetrakis(t-butyl isocyanide)rhodium Tetrafluoroborate, (II; R = Et).—(a) *With propylamine.* Similarly (II; R = Et) (0.20 g, 0.29 mmol) and propylamine (5 cm^3) reacted (1 h) to give after recrystallisation pale yellow *crystals* of (IV; R = $\mathrm{Pr^n}$) (0.13 g, 60%), m.p. 124 °C (decomp.) (Found: C, 40.3; H, 6.6; N, 9.3. $\mathrm{C_{25}H_{50}BF_4IN_5Rh}$ requires C, 40.7; H, 6.8; N, 9.5%), 3 220m (NH), 3 195w (NH), 2 205s (NC), 2 185s (NC), and 1 545s cm^{-1} ($\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}$). The ^{1}H n.m.r. spectrum (in $\mathrm{CDCl_3}$) showed resonances at τ 2.10 (sbr, 2 H, $\mathrm{N}H\mathrm{Bu^t}$), 6.29 [t, 2 H, $\mathrm{N}CH_2$, *J*(HH) 6.0 Hz], 8.13 [qd, 2 H, $\mathrm{Rh}CH_2$, *J*(HH) 7.0, *J*(RhH) 2.0 Hz], 8.3—8.5 (complex m, 4 H, $\mathrm{NCH_2}CH_2CH_2$), 8.37 (s, 18 H, $\mathrm{NBu^t}$), 8.45 (s, 18 H, $\mathrm{NBu^t}$), 8.73 [td, 3 H, $\mathrm{RhCH_2}CH_3$, *J*(HH) 7.0, *J*(RhH) 2.0 Hz], and 9.01 [t, 3 H, $\mathrm{NCHCH_2}CH_3$, *J*(HH) 6.0 Hz].

(b) *With butylamine.* In a similar manner treatment of (II; R = Et) (0.20 g, 0.29 mmol) with butylamine (5 cm^3) afforded yellow *crystals* of (IV; R = $\mathrm{Bu^n}$) (0.14 g, 63%), m.p. 150—153 °C (decomp.) (Found: C, 42.1; H, 7.0; N, 9.3. $\mathrm{C_{26}H_{52}IN_5Rh}$ requires C, 41.5; H, 6.9; N, 9.3%), 3 278m (NH), 3 120w (NH), 2 201s (NC), 2 185s (NC), and 1 545m cm^{-1} ($\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}$). The ^{1}H n.m.r. spectrum (in $\mathrm{CDCl_3}$) showed resonances at τ 2.87 (sbr, 2 H, $\mathrm{N}H\mathrm{Bu^t}$), 6.29 [t, 2H, $\mathrm{N}CH_2$, *J*(HH) 6.0 Hz], 8.15 [qd, 2 H, $\mathrm{Rh}CH_2$, *J*(HH) 7.0, *J*(RhH) 2.0 Hz], 8.3—8.5 (complex m, $\mathrm{NCH_2}CH_2CH_3$), 8.37 (s, 18 H, $\mathrm{NBu^t}$), 8.42 (s, 18 H, $\mathrm{NBu^t}$), 8.76 [td, 3 H, $\mathrm{RhCh_2}CH_3$, *J*(HH) 7.0, *J*(RhH) 2.0 Hz], and 9.10 [t, 3 H, $\mathrm{CH_2}CH_3$, *J*(HH) 6.0 Hz].

Reaction of Iodomethyl[propylamino(t-butylamino)carbene]-bis(t-butyl isocyanide)rhodium(III) *Tetrafluoroborate,* (VI), *with Propylamine.*—A suspension of (VI) (0.20 g, 0.28 mmol) in propylamine (5 cm^3) was stirred at room temperature to afford (0.5 h) a clear yellow solution. Removal of the excess of amine *in vacuo* and recrystallisation of the residue from methylene chloride–diethyl ether afforded pale yellow crystals of (III; R′ = $\mathrm{Pr^n}$) (0.15 g, 75%) identical (i.r. and ^{1}H n.m.r. spectroscopy) to that described previously.

Preparation of Methylpentakis(t-butyl isocyanide)rhodium-(III) *Bis(tetrafluoroborate).*—An excess of t-butyl isocyanide (0.1 cm^3) was added to a stirred solution of methyltetrakis-(t-butyl isocyanide)rhodium(III) bis(tetrafluoroborate) (0.14 g, 0.23 mmol) in methylene chloride. After 24 h at room temperature the solvent was removed *in vacuo*, and the residue recrystallised from methylene chloride–diethyl ether to give white crystals of *methylpentakis(t-butyl isocyanide)-rhodium bis(tetrafluoroborate)* (0.08 g, 53%), m.p. 117—118 °C (decomp.) (Found: C, 44.0; H, 6.8; N, 10.1. $\mathrm{C_{26}H_{48}B_2F_8N_5Rh}$ requires C, 44.1; H, 6.8; N, 9.9%), 2 238vs cm^{-1} (NC). The ^{1}H. n.m.r. spectrum (in $\mathrm{CD_2Cl_2}$) showed resonances at τ 8.36 (s, 45 H, $\mathrm{N}Bu^t$) and 9.08 [d, 3 H, Rh*Me*, *J*(RhH) 1.7 Hz].

Reaction of $[\mathrm{RhMe(CNBu^t)_5}][\mathrm{BF_4}]_2$ *with Methylamine.*—An excess of methylamine (5 cm^3) was condensed (−196 °C) into a Carius tube containing $[\mathrm{RhMe(CNBu^t)_5}][\mathrm{BF_4}]_2$ (0.10 g, 0.14 mmol). The reaction produced a pale yellow solution after 45 min at room temperature when the tube was opened and excess of amine removed *in vacuo*. Recrystallisation from methylene chloride–diethyl ether afforded white *crystals* of (V) (0.06 g, 60%), m.p. 163–165 °C (decomp.) (Found: C, 44.2, H, 7.2; N, 11.5. $\mathrm{C_{27}H_{53}B_2F_8N_6Rh}$ requires C, 43.9; H, 7.2; N, 11.4%), 3 290m (NH), 3 260m(sh) (NH), 3 235m(sh) (NH), 2 229s (NC), 2 209s (NC), and 1 560s cm^{-1} ($\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N}$). The ^{1}H n.m.r. spectrum (in $\mathrm{CDCl_3}$) showed resonances at τ 4.22 (sbr, 2 H, $\mathrm{N}H\mathrm{Bu^t}$), 6.90 (s, 3 H, N*Me*), 8.42 (s, 27 H, $\mathrm{NBu^t}$), 8.48 (s, 18 H, $\mathrm{NBu^t}$), and 9.65 [d, 3 H, Rh*Me*, *J*(RhH) 2.0 Hz].

Reaction of (II; R = Me) *with Hydrazine.*—Anhydrous hydrazine (1 cm^3) was added to a solution of (II; R = Me)

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(0.30 g, 0.45 mmol) in methanol (10 cm^3) and stirred at room temperature (0.5 h). Removal of the solvent ***in vacuo*** afforded a yellow solid which, on recrystallisation from acetone–diethyl ether, gave yellow crystals of [1,4-***bis***(*t-butylamino*)-2,3-*diazabutanediylidene*]*iodo*(*methyl*)***bis***(*t-butyl isocyanide*)*rhodium*(III) ***tetrafluoroborate***, (VII); (0.20 g, 63%), m.p. 155 °C (decomp.) (Found: C, 36.0; H, 6.1; N, 12.0. $C_{21}H_{43}BF_4IN_6Rh$ requires C, 36.2; H, 6.2; N, 12.1%), 3 442m (NH), 3 320s br (NH), 2 198s (NC), 2 174s (NC), and 1 570vs cm^{-1} ($N\cdots C\cdots N$). The ^1H n.m.r. spectrum (in $CDCl_3$) showed resonances at τ 0.77 (mbr, 2 H, N*H*N*H*), 4.23 (s, 2 H, N*H*Bu^t), 8.43 (s, 18 H, NBu^t), 8.58 (s, 18 H, NBu^t), and 9.57 [d, 3 H, Rh*Me*, *J*(RhH) 2.0 Hz].

Preparation of Bis(2,2′-*bipyridyl or* 1,10-*phenanthroline*)-*bis*(*isocyanide*)*iron*(II) *Bis*(*hexafluorophosphate*).—The following general procedure was adopted. A solution of isocyanide (1 cm^3) and $[Fe(bipy)_3][PF_6]_2$ or $[Fe(phen)_3][PF_6]_2$ in acetone (15 cm^3) was heated under reflux (5 min) affording yellow-orange solutions. The product was precipitated on addition of light petroleum (b.p. 40—60 °C) and was recrystallised from methylene chloride–hexane.

Reaction of $[Fe(CNMe)_2(bipy)_2][PF_6]_2$, (VIII; R = Me) *with Methylamine*.—An excess of methylamine (8 cm^3) was condensed into a tube containing (VIII; R = Me) (0.43 g, 0.8 mmol). The complex gradually dissolved forming a dark green solution after 24 h at room temperature. Removal of the excess of methylamine afforded a purple solid, which on recrystallisation from acetone–diethyl ether gave dark purple crystals of *bis*(2,2′-*bipyridyl*)[2-*methyl*-1,3-*dimethylamino*)-2-*azapropanediylidene*]*iron*(II) *bis*(*hexafluorophosphate*), (X) (0.38 g, 78%), m.p. 241 °C (decomp.) (Found: C, 45.4; H, 4.4; N, 15.2. $C_{35}H_{27}F_{12}FeN_7P_2$ requires C, 45.2; H, 4.1; N, 15.0%), 3 300s (NH) and 1 570s cm^{-1} ($N\cdots C\cdots N$).

Reaction of $[Fe(CNPr^i)_2(bipy)_2][PF_6]_2$, (VIII; R = Pr^i) *with Methylamine*.—In a similar manner, reaction of (VIII; R = Pr^i) with methylamine (8 cm^3) afforded purple *crystals* of (XI) (0.38 g, 74%), m.p. 245 °C (decomp.) (Found: C, 41.6; H, 4.5; N, 11.6. $C_{29}H_{35}F_{12}FeN_7P_2$ requires C, 42.0; H, 4.2; N, 11.8%), 3 300s (NH) and 1 540s cm^{-1} ($N\cdots C\cdots N$).

Reaction of $[Fe(CNPr^i)_2(phen)_2][PF_6]_2$, (IX; R = Pr^i) *with Methylamine*.—Similarly, treatment of (IX; R = Pr^i) with methylamine afforded, on recrystallisation from acetone–diethyl ether, dark purple *crystals* of (XII) (0.18 g, 85%), m.p. 251 °C (decomp.) (Found: C, 51.9; H, 5.1; N, 12.6. $C_{33}H_{28}F_8FeN_7P_2$ requires C, 52.2; H, 4.7; N, 12.8%), 3 220m (NH), 3 260m (NH), and 1 550s cm^{-1} ($N\cdots C\cdots N$).

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