Reactivity of the Rhodium(III) Formamidinato-complex $[Rh(\eta\text{-}C_5Me_5)Cl(p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p)]$ with CO and Heterocumulenes. Crystal and Molecular Structure of the Thioureido-complex $[Rh(\eta\text{-}C_5Me_5)Cl\{PhN \overset{\cdots}{-} C[N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p] \overset{\cdots}{-} S\}]$ *

Pasquale Piraino, Giuseppe Bruno, Giuseppe Tresoldi, Giovanni Faraone, and Gabriella Bombieri
Istituto di Chimica Generale dell'Università, 98100 Messina, Italy

The complex $[Rh(\eta\text{-}C_5Me_5)Cl(p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p)]$ reacts with CO, CS_2, and PhNCS giving respectively the carbamoyl $[Rh(\eta\text{-}C_5Me_5)Cl\{CO\text{-}N(C_6H_4Me\text{-}p)CH{=}NC_6H_4Me\text{-}p\}]$, dithiocarbamato- $[Rh(\eta\text{-}C_5Me_5)Cl\{S \overset{\cdots}{-} C[N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p] \overset{\cdots}{-} S\}]$, and thioureido-complexes $[Rh(\eta\text{-}C_5Me_5)Cl\{PhN \overset{\cdots}{-} C[N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p] \overset{\cdots}{-} S\}]$ *via* formal insertion into the Rh–N bond. The structure of the thioureido-complex has been determined by single-crystal *X*-ray diffraction: space group $P\bar{1}$ with $a = 9.339(2)$, $b = 12.130(3)$, $c = 13.950(3)$ Å, $\alpha = 95.7(1)$, $\beta = 96.3(1)$, $\gamma = 103.9(1)^\circ$, and $Z = 2$. Refinement on the basis of the 3 225 observed reflections $[I \geqslant 2\sigma(I)]$ gave a final conventional R value of 0.046 (R' = 0.046). The molecule contains the four-membered chelate ring $\overline{Rh\text{-}N\text{-}C\text{-}S}$. The C–N and C–S bonds [1.299(8) and 1.741(6) Å] have a considerable double-bond character with a higher percentage for the former.

The chemistry of heterocumulenes such as CS_2, PhNCO, PhNCS, and COS with transition-metal complexes is still of current interest. Besides the normal modes of co-ordination, σ or η^2, they can undergo the reactions of dimerization,[1] disproportionation,[2] or insertion into an M–X bond (X = H, N, or C).[3]

The insertion reactions of heterocumulenes into M–N bonds previously reported mainly concern amido-derivatives of early transition metals.[4] Insertion reactions of CS_2 into the Ni–N bond of cationic nickel amine and tetra-aziridine complexes were also studied.[5]

We have previously reported [6] on reactions of the formamidinatorhodium(I) complex $[\{Rh(C_8H_{12})(p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p\}_2]$ with CO and heterocumulenes such as CS_2, PhNCO, and PhNCS. These reactions occur with diene displacement rather than interaction with the Rh–N bond. We have now investigated the reactions of the same ligands with the formamidinatorhodium(III) derivative $[Rh(\eta\text{-}C_5Me_5)Cl(p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p)]$ in which the C_5Me_5 acts as a protecting ligand, and have synthesized carbamoyl, dithiocarbamato-, and thioureido-rhodium(III) complexes by formal insertion of CO, CS_2, and PhNCS respectively into the Rh–N bond.

Results and Discussion

The complex $[Rh(\eta\text{-}C_5Me_5)Cl(p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p)]$ (1) was prepared by refluxing for 6 h a toluene solution of $K[p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p]$ with $[\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2]$ (molar ratio 2 : 1). Work up of the resultant solution as described in the Experimental section gave complex (1) in high yields. The ^1H n.m.r. spectrum of (1), which is a monomer in benzene, shows that the formamidine is probably symmetrically chelated to the rhodium. It displays, in the methyl region, only two sharp signals at τ 8.3 and 7.73 (ratio 2.5 : 1) assigned respectively to the C_5Me_5 and tolyl methyl groups. A doublet at τ 1.68 [J(Rh–H) = 3.6 Hz] was assigned to the resonance of the methine proton. The i.r. spectrum of complex (1) shows the asymmetric $N \overset{\cdots}{-} C \overset{\cdots}{-} N$ vibration at 1 548 cm^{-1}, indicative of extensive electronic delocalization along the NCN moiety.

Reaction with CO.—Carbon monoxide was bubbled for 3 h, at room temperature, through a chloroform solution of complex (1). The red colour of the starting solution was unchanged. After evaporation of the solvent the crude product was chromatographed on an Al_2O_3 column with CH_2Cl_2 as mobile phase. Elution with diethyl ether gave the pure red-orange complex $[Rh(\eta\text{-}C_5Me_5)Cl\{CO\text{-}N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p\}]$ (2). Analytical data and spectral properties (Table 1) suggested the formation of a carbamoyl derivative by formal insertion of carbon monoxide into the Rh–N bond.

The ^1H n.m.r. spectrum of (2) shows, besides the resonance of the C_5Me_5 group at τ 8.55, a doublet at τ 2.46 [J(Rh–H) = 1.7 Hz] and a couple of singlets at τ 7.71 and 7.68. The doublet arises from the coupling of the methine proton of the formamidine with the rhodium atom and lies upfield respect to the formamidine parent as found for other carbamoyl complexes.[7,8] The singlets are assigned to the methyl groups and indicate that the formal insertion of CO into the Rh–N bond has led to loss of symmetry of the formamidine fragment as expected for a carbamoyl derivative. The i.r. spectrum exhibits, in the range 1 500—1 700 cm^{-1}, bands at 1 670vs and 1 620s cm^{-1} assigned to the carbamoyl carbonyl and the C=N stretch.

The few acyl-triazenido- and -formamidinato-complexes previously reported were obtained by interaction between the formamidinato- or triazenido-anion with a CO group of a carbonyl complex;[7] some of these undergo, under forcing conditions, decarbonylation, reforming the heteroallylic fragment. Interaction with external CO was achieved reversibly with the triazenido-complex $[Ir(CO)(RN \overset{\cdots}{-} N \overset{\cdots}{-} NR)(PPh_3)]$ (R = p-tolyl) while the analogous rhodium(I) derivative fails to react with CO.[9] Concerning formamidinato-derivatives, the only reported example is $[(Ph_3P)_2(OCNR\text{-}CHNR')(OC)IrAg(CO)Cl]$ (R = Bu^t, Pr^i, or C_6H_{11}; R′ =

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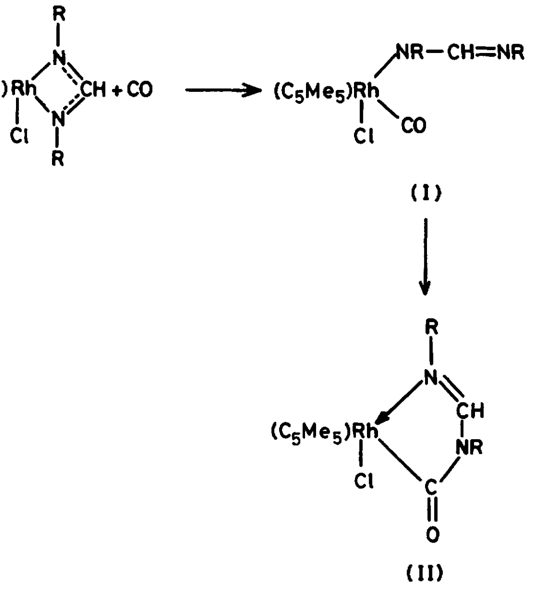
* Chloro(η-pentamethylcyclopentadienyl)(N-phenyl-N'-p-tolyl-N'-p-tolyliminomethylthioureido-NS)rhodium(III).

Supplementary data available (No. SUP 23677, 24 pp.): thermal parameters, H-atom positions, complete interatomic distances and angles, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected i.r. and ^1H n.m.r. data

Complex	I.r. (cm^{-1}, Nujol mull) $\nu(C{=}N)$	$\nu(C \underline{\cdot\cdot\cdot} N)$	Others	^1H N.m.r. (τ, $CDCl_3$) C_5Me_5	CH_3	CH
(1) $[Rh(\eta\text{-}C_5Me_5)Cl(p\text{-}MeC_6H_4N \underline{\cdot\cdot\cdot} CH \underline{\cdot\cdot\cdot} NC_6H_4Me\text{-}p)]$			1 548 $[\nu_{asym}(NCN)]$	8.3 (s)	7.73 (s)	1.68 (d)[a]
(2) $[Rh(\eta\text{-}C_5Me_5)Cl\{CO{-}N(C_6H_4Me\text{-}p){-}CH{=}NC_6H_4Me\text{-}p\}]$	1 620s		1 670s $[\nu(CO)]$	8.55 (s)	7.71 (s), 7.68 (s)	2.46 (d)[b]
(3) $[Rh(\eta\text{-}C_5Me_5)Cl\{PhN \underline{\cdot\cdot\cdot} C[N(C_6H_4Me\text{-}p){-}CH{=}NC_6H_4Me\text{-}p] \underline{\cdot\cdot\cdot} S\}]$	1 650vs	1 555s, 1 530s		8.47 (s)	7.78 (s), 7.82 (s)	1.98 (s)
(4) $[Rh(\eta\text{-}C_5Me_5)Cl\{S \underline{\cdot\cdot\cdot} C[N(C_6H_4Me\text{-}p){-}CH{=}NC_6H_4Me\text{-}p] \underline{\cdot\cdot\cdot} S\}]$	1 635s	1 520m		8.22 (s)	7.6 (s), 7.68 (s)	0.85 (s)

[a] $J(Rh{-}H) = 3.6$ Hz. [b] $J(Rh{-}H) = 1.7$ Hz.



Scheme.

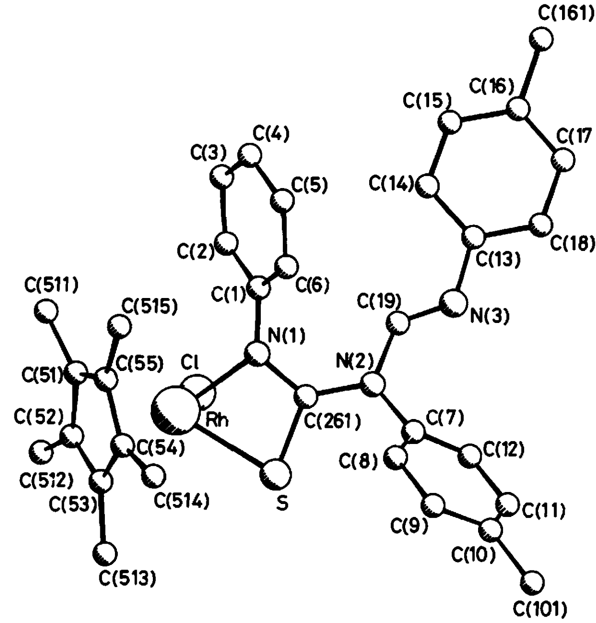


Figure. View of complex (3) down *a*

p-tolyl) obtained by reaction of carbon monoxide with the complex $[(Ph_3P)_2(OC)IrAg(RN \underline{\cdot\cdot\cdot} CH \underline{\cdot\cdot\cdot} NR)Cl]$.[10]

Mechanisms for the above mentioned reactions were suggested involving, as a first step, nucleophilic attack of the imino-nitrogen or formamidinato-anion upon a carbonyl group [7a,8] as well as insertion of carbon monoxide into the M–N bond.[7c,9] In any case, the presence of a carbonyl co-ordinated to the rhodium seems necessary.

We suggest that the formal insertion of CO into the Rh–N bond of complex (1) takes place as in the Scheme. For the formation of the carbamoyl derivatives, which are postulated as intermediates during the catalytic carbonylation of amines by carbonyl complexes, it was suggested that only carbonyls with ν(CO) higher than 2 000 cm^{-1} can undergo nucleophilic attack by amines.[11] The intermediate (I), a rhodium(III) carbonyl complex, ought to exhibit ν(CO) at frequencies higher than 2 000 cm^{-1} and then could undergo nucleophilic attack from the imino-nitrogen.

Reaction with PhNCS.—A benzene solution of complex (1) reacts, at reflux temperature, with an excess of PhNCS to give, as described in the Experimental section, red-orange crystals of the thioureido-derivative $[Rh(\eta\text{-}C_5Me_5)Cl\{PhN \underline{\cdot\cdot\cdot} C[N(C_6H_4Me\text{-}p){-}CH{=}NC_6H_4Me\text{-}p] \underline{\cdot\cdot\cdot} S\}]$ (3) arising from formal insertion of PhNCS into the Rh–N bond. The compound is a monomer in benzene solution and non-conducting in acetone. The assignment of the structure was made by i.r. and ^1H n.m.r. spectral data and confirmed by single-crystal *X*-ray diffraction.

The ^1H n.m.r. spectrum is easily interpreted and consists of three sharp alkyl resonances at τ 8.47, 7.78, and 7.82 and a methine proton at τ 1.98 uncoupled with the rhodium atom. The singlet at τ 8.47 was assigned to the C_5Me_5 and those at τ 7.78 and 7.82 to the tolyl methyls, *i.e.* a non-equivalent methyl environment. The i.r. spectrum, showing no bands in the region 2 000—2 200 cm^{-1}, allows one to rule out the presence of a σ-co-ordinated heterocumulene. Strong bands at 1 650, 1 555, and 1 530 cm^{-1} were assigned, respectively, to the vibrations $\nu(C{=}N)$ and $\nu(C \underline{\cdot\cdot\cdot} N)$. The values for the latter lie in the range found for the few thioureido-complexes reported [12,13] and are dependent on the double-bond character of the $C \underline{\cdot\cdot\cdot} N$ bond.

To verify that the PhNCS had inserted into the Rh–N bond an *X*-ray analysis of complex (3) was undertaken. The solid-state structure, shown in the Figure, confirms the discrete monomeric nature of $[Rh(\eta\text{-}C_5Me_5)Cl\{PhN \underline{\cdot\cdot\cdot} C[N(C_6H_4Me\text{-}p){-}CH{=}NC_6H_4Me\text{-}p\}] \underline{\cdot\cdot\cdot} S\}]$. The Rh^{III} is co-ordinated by the chlorine ion, sulphur and nitrogen atoms of the thioureido-ligand, and the η^5-bonded pentamethylcyclopentadienyl ligand. The final positional para-

Table 2. Atomic co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	1 662(1)	496(0)	2 242(0)	C(2)	1 691(4)	1 315(3)	4 800(3)
Cl	−923(2)	360(1)	2 326(1)	C(3)	2 110(4)	1 311(3)	5 791(3)
S	1 929(2)	2 249(1)	1 506(1)	C(4)	3 448(4)	2 037(3)	6 263(3)
N(1)	2 181(6)	1 951(4)	3 268(3)	C(5)	4 369(4)	2 727(3)	5 744(3)
N(2)	2 422(6)	3 925(4)	3 051(3)	C(6)	3 951(4)	2 770(3)	4 753(3)
N(3)	2 441(6)	5 265(4)	4 363(4)	C(7)	3 124(4)	4 759(3)	2 479(3)
C(261)	2 225(7)	2 778(5)	2 738(4)	C(8)	4 510(4)	4 737(3)	2 205(3)
C(19)	2 006(7)	4 257(6)	3 946(4)	C(9)	5 167(4)	5 516(3)	1 611(3)
C(51)	1 959(11)	−1 099(7)	2 669(6)	C(10)	4 437(4)	6 317(3)	1 290(3)
C(52)	1 316(8)	−1 272(6)	1 676(6)	C(101)	5 190(11)	7 170(8)	655(6)
C(53)	2 305(10)	−596(7)	1 161(5)	C(11)	3 051(4)	6 339(3)	1 564(3)
C(54)	3 574(8)	3(6)	1 840(6)	C(12)	2 395(4)	5 560(3)	2 158(3)
C(55)	3 343(11)	−337(7)	2 751(6)	C(13)	2 058(5)	5 494(3)	5 321(3)
C(511)	1 354(15)	−1 737(9)	3 466(9)	C(14)	1 850(5)	4 685(3)	5 971(3)
C(512)	−185(10)	−2 085(8)	1 271(9)	C(15)	1 638(5)	5 006(3)	6 923(3)
C(513)	2 043(13)	−564(10)	86(6)	C(16)	1 635(5)	6 137(3)	7 225(3)
C(514)	4 938(10)	795(9)	1 562(9)	C(161)	1 499(10)	6 491(9)	8 281(6)
C(515)	4 477(14)	106(11)	3 652(7)	C(17)	1 843(5)	6 946(3)	6 575(3)
C(1)	2 612(4)	2 044(3)	4 281(3)	C(18)	2 054(5)	6 624(3)	5 623(3)

Table 3. Selected distances (Å) and angles (°) with e.s.d.s in parentheses

Rh–Cl	2.397(2)	N(1)–Rh–Cl	88.5(2)
Rh–S	2.423(2)	N(1)–Rh–S	67.3(1)
Rh–N(1)	2.082(5)	S–Rh–Cl	91.5(1)
Rh–C(51)	2.152(7)	Rh–S–C(261)	78.7(2)
Rh–C(52)	2.146(7)	Rh–N(1)–C(261)	103.2(4)
Rh–C(53)	2.139(7)	Rh–N(1)–C(1)	128.5(4)
Rh–C(54)	2.128(7)	C(261)–N(1)–C(1)	127.6(5)
Rh–C(55)	2.157(8)	N(1)–C(261)–N(2)	127.6(6)
S–C(261)	1.741(6)	N(2)–C(261)–S	121.7(5)
N(1)–C(261)	1.299(8)	N(1)–C(261)–S	110.7(5)
N(1)–C(1)	1.412(6)	C(19–N(2)–C(261)	119.6(5)
N(2)–C(19)	1.398(8)	C(7)–N(2)–C(261)	119.3(5)
N(2)–C(261)	1.378(8)	C(19)–N(2)–C(7)	121.0(5)
N(2)–C(7)	1.431(7)	N(3)–C(19)–N(2)	122.2(6)
N(3)–C(19)	1.252(8)	C(19)–N(3)–C(13)	117.6(5)
N(3)–C(13)	1.439(7)		
C–C (C_5Me_5, av.)	1.40(1)		
C–CH_3 (av.)	1.51(1)		

Table 4. Least-squares planes with deviations (Å) of the relevant atoms in square brackets. The equation of a plane in direct space is given by $PX + QY + RZ = S$

	P	*Q*	*R*	*S*
	−6.0790	10.5679	2.2037	−1.7721
Plane 1: C(51)—C(55) (C_5Me_5) [C(51) 0.008, C(52) −0.003, C(53) −0.003, C(54) 0.008, C(55) −0.010, C(511) −0.123, C(512) −0.039, C(513) −0.047, C(514) −0.045, C(515) −0.037, Rh 1.780]	8.6832	1.5280	−0.9834	1.8705
Plane 2: C_5Me_5 gravity centre, N(1), S(1) [Rh −0.572, Cl −2.846]	−6.4674	10.1292	2.7648	1.5649
Plane 3: C(1)—C(6) (phenyl)	2.0303	5.7796	9.8180	5.8185
Plane 4: C(7)—C(12) (phenyl)	9.0447	−0.4524	0.1766	1.8655
Plane 5: Thioureido-fragment N(1), C(261), S(1), N(2), C(19), N(3), C(13) [N(1) 0.077, C(261) 0.070, S(1) −0.196, N(2) 0.201, C(19) −0.174, N(3) 0.181, C(13) −0.159]	8.7816	−0.5430	2.1343	2.6445
Plane 6: C(13)—C(18) (phenyl)				

Dihedral angles (°)

1–2	71	1–3	4	2–3	68	1–4	66
2–4	62	3–4	67	1–5	63	2–5	10
3–5	60	4–5	64	5–6	8	2–6	15

meters of the non-hydrogen atoms are given with estimated standard deviations in Table 2, selected bond distances and angles in Table 3. Least-squares mean planes and atomic displacements therefrom are given for structurally significant groupings of atoms along with selected dihedral angles in Table 4.

While the co-ordination number of the rhodium is six (assuming the η^5-C_5Me_5 ligand occupies three co-ordination sites) the parameters in Table 3 indicate a pseudo-tetrahedral geometry if the η^5-bonded C_5Me_5 ligand is regarded as occupying a single polyhedral vertex. A more pictorial description of this kind of geometry is a three-legged piano stool.

The rhodium atom is 0.572 Å away from the plane defined by the centre of gravity of the cyclopentadienyl ring and the sulphur and the nitrogen of the thioureido-ligand, whereas the chlorine atom is displaced on the same side by 2.846 Å. The thioureido-ligand is nearly planar. The deviations from the best mean plane (Table 4) are of the same order as those reported for the thioureido-ligand in the complex chloro-(*N*,*N*-dimethylthiocarbamoyl)(*N*,*N*′-dimethyl-*N*′-phenylthioureido)triphenylphosphinerhodium(III).[14]

The phenyl rings attached to N(1) and N(2) are twisted with respect to this plane by 60 and 64° respectively, while that attached to N(3) is nearly coplanar. In this situation no significant π overlap for N(1) with the attached aromatic system is present, N(1)–C(1) having a single bond distance of 1.412(6) Å. The same is true of the N(2) atom where N(2)–C(7) (phenyl) is 1.431(7) Å and it is justified by the value of the dihedral angle of the phenyl ring with the thioureido-fragment. However, rather unexpected is the single-bond value for N(3)–C(13) (phenyl) where the aromatic system is nearly coplanar with the thioureido-fragment. The N(3)–

C(19) bond distance [1.252(8) Å] is typical of a double bond. As a consequence, no significant electron delocalization seems to be present in this system.

The orientation of the phenyl groups is such as to avoid short contacts with adjacent atoms; the closest distances within the thioureido-ligand are C(19) $\cdots$ C(6) 3.058 Å and C(8) $\cdots$ S(1) 3.357 Å. The pentamethylcyclopentadienyl ligand is nearly parallel to the nearest phenyl group [C(1)—C(6)], dihedral angle 4°, in order to attain a better molecular packing.

The value of 2.082(5) Å for the Rh–N(1) distance compares favourably with that [2.124(12) Å] reported for the above named thioureido-complex [14] and corresponds to the values reported for a single Rh^{III}–N(sp^2) bond.[15,16] The Rh–S bond [2.423(2) Å] is longer than the corresponding Rh–S(2) distance [2.371(5) Å] found in ref. 14 for the thioureido-fragment and is closer to the Rh–S(1) values of the thiocarbamoyl fragment [2.419(5) Å] detected in the same compound and in [$RhCl(S_2CNMe_2)(SCNMe_2)(PPh_3)$] [Rh–S(1) 2.432(5) Å].[12a] The four-membered chelate ring has bond distances and angles comparable with those in ref. 14 with N(1)–C(261) [1.299(8) Å] and S–C(261) [1.741(6) Å] having, as expected, considerable double-bond character and a higher percentage for the former.[17]

The Rh atom lies 1.78 Å away from the best plane through the atoms of the C_5Me_5 ring, comparable to values observed in related complexes.[18–20] The C_5 ring is nearly coplanar with the Me carbon atoms while their distances from the mean plane of the ring range from 0.04 to 0.12 Å. These deviations are in any case in the opposite sense to that of the rhodium.

The Rh–Cl bond distance [2.397(2) Å] is somewhat shorter than the values reported for rhodium thiocarbamoyl complexes [12a,14] where however a *trans* influence from the carbon attached to the rhodium is present, but it is comparable with the values 2.357(18)—2.362(16) and 2.380(16) Å found in [$\{Rh(\eta\text{-}C_5Me_5)\}_3Cl_5(CH_2CMe_3)_3$]$PF_6$.[18]

Reaction with CS_2.—Reaction of complex (1) in neat CS_2 for 6 h at room temperature led to a deep red solution from which was isolated the dithiocarbamato-complex [$Rh(\eta\text{-}C_5Me_5)Cl\{S \overset{\cdots}{-} C[N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p] \overset{\cdots}{-} S\}$] (4) which also can be considered as formed by formal insertion of CS_2 into the Rh–N bond. The complex is a monomer in benzene solution and non-conducting in acetone. The formulation as a dithiocarbamato-derivative is based on analytical data and on the analogy of its spectral data with those of the thioureido-complex (3).

The ^1H n.m.r. spectrum of (4) shows, like the thioureido-complex, the methine proton as a sharp singlet at τ 0.85, methyl signals as singlets at τ 7.6 and 7.68, and the C_5Me_5 resonance at τ 8.22 (ratio 1 : 6 : 15). Infrared bands at 1 635 and 1 520 cm^{-1} were assigned respectively to the ν(C=N) and ν(C $\overset{\cdots}{-}$ N) stretches.

Concerning insertion reactions of heterocumulenes into M–N bonds, no mechanistic studies have been carried out and the only mechanism suggested involves nucleophilic attack of the lone pair of the nitrogen on the electrophilic centre of the heteroallene.[21,22] In the absence of experimental data we cannot say which mechanism is operative during the formation of the complexes (3) and (4), although the formation of an intermediate of type (I), Scheme, in which the heterocumulene is σ bonded to the rhodium atom is possible.

It is worthwhile mentioning that CS_2 σ-bonded complexes of Rh, Ir,[23] Os,[24] and Pt [25] have been isolated or suggested from kinetic data, while σ-SCNPh complexes were suggested as intermediates during the reaction of [$Rh(PPh_3)_3Cl$] with aryl and aroyl isocyanates.[26,27]

Reactions with COS *and* CO_2.—Attempts to obtain carbamato- or monothiocarbamato-derivatives by insertion of CO_2 or COS into the Rh–N bond of complex (1) were unsuccessful. When a toluene solution of (1) was saturated with COS for 15 min and left, with stirring, for 20 h a white precipitate was formed containing mainly unbonded formamidine. From the solution a red compound was recovered which, despite several attempts at fractional crystallization or chromatography, could not be isolated pure. The ^1H n.m.r. spectrum of the compound contains, in the methyl region, only a sharp singlet arising from the C_5Me_5 resonance showing that this reaction occurs with formamidine displacement.

Carbon dioxide, because of its inertness, fails to react, at atmospheric pressure, with complex (1) but it is possible that it would do so under more forcing conditions.

Experimental

The compounds [$\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2$] and *N*,*N*′-di-*p*-tolylformamidine were prepared using published methods.[28,29] Phenyl isocyanate was distilled prior to use. Benzene was distilled under nitrogen and stored over molecular sieves. Infrared spectra were obtained using a Perkin-Elmer 457 spectrophotometer and ^1H n.m.r. spectra using a Perkin-Elmer R 24B at 60 MHz. Microanalyses were performed by the Laboratory of Organic Chemistry Institute, University of Milan and by Bernhardt Laboratorium, Elbach, West Germany. Molecular weights were determined with a Knauer vapour-pressure osmometer. All the reactions were carried out under dry nitrogen.

Preparations.—[$Rh(\eta\text{-}C_5Me_5)Cl(p\text{-}MeC_6H_4N \overset{\cdots}{-} CH \overset{\cdots}{-} NC_6H_4Me\text{-}p)$]. The salt K[$CH(NC_6H_4Me\text{-}p)_2$] (0.42 g, 1.6 mmol), generated *in situ* by treating a toluene solution of *N*,*N*′-di-*p*-tolylformamidine with the stoicheiometric amount of $KOBu^t$, was heated under reflux for 6 h with [$\{Rh(\eta\text{-}C_5Me_5)Cl_2\}_2$] (0.5 g, 0.8 mmol). The red solution obtained was filtered and evaporated to dryness. The residue was recrystallized twice from benzene–n-heptane (1 : 3) to give 0.7 g of the red complex (1) [Found: C, 60.0; H, 6.2; Cl, 7.2; N, 5.45%; *M* (benzene) 520. $C_{25}H_{30}ClN_2Rh$ requires C, 60.45; H, 6.1; Cl, 7.15; N, 5.65%; *M* 496.87].

[$Rh(\eta\text{-}C_5Me_5)Cl\{CO\text{-}N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p\}$]. Carbon monoxide was bubbled through a chloroform solution of complex (1) (0.3 g) for 3 h, the starting colour being unchanged. The solution was evaporated and chromatographed on a column of Al_2O_3 in CH_2Cl_2. Elution of a red band with diethyl ether gave a yellow-orange solution which was partially evaporated, in the presence of n-heptane, to give the red-orange complex (2) (35% yield) [Found: C, 59.6; H, 5.7; Cl, 6.7; N, 5.25%; *M* (benzene) 540. $C_{26}H_{30}ClN_2ORh$ requires C, 59.5; H, 5.75; Cl, 6.75; N, 5.35%; *M* 524.87].

[$Rh(\eta\text{-}C_5Me_5)Cl\{PhN \overset{\cdots}{-} C[N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4\text{-}Me\text{-}p] \overset{\cdots}{-} S\}$]. Complex (1) (0.3 g, 0.6 mmol) and freshly distilled PhNCS (0.13 g, 1 mmol) were heated under reflux for 3 h. The deep red solution was concentrated to 5—10 cm^3 and n-heptane was added affording the orange complex (3). The mother-liquors were left overnight, depositing a crop of crystals suitable for the *X*-ray examination. Total yield 45% [Found: C, 60.3; H, 5.75; Cl, 5.4; N, 6.5; S, 5.35%; *M* (benzene) 601. $C_{32}H_{35}ClN_3RhS$ requires C, 60.8; H, 5.6; Cl, 5.6; N, 6.65; S, 5.05%; *M* 632.06].

[$Rh(\eta\text{-}C_5Me_5)Cl\{S \overset{\cdots}{-} C[N(C_6H_4Me\text{-}p)\text{-}CH{=}NC_6H_4Me\text{-}p] \overset{\cdots}{-} S\}$]. Complex (1) was allowed to react in neat CS_2, at room temperature, for 6 h. The red solution was evaporated to dryness and recrystallized from benzene–n-heptane (1 : 3) affording 0.13 g of complex (4) [Found: C, 54.6; H, 5.3; Cl, 6.2; N, 4.8; S, 11.05%; *M* (benzene) 553. $C_{26}H_{30}ClN_2$-

RhS_2 requires C, 54.5; H, 5.25; Cl, 6.2; N, 4.9; S, 11.2%; *M* 573].

X-Ray Data Collection and Structure Determination.—Suitable crystals of complex (3) of prismatic habit were obtained from benzene–n-heptane. A crystal of dimensions *ca.* $0.11 \times 0.13 \times 0.17$ mm was selected and mounted on a Siemens-Stoe automatic four-circle diffractometer. Accurate unit-cell dimensions and crystal orientation matrices together with their estimated standard errors were obtained from least-squares refinement of the 2θ, ω, χ, and φ values of 20 carefully centred high-angle reflections using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å).

Intensity data were collected, at room temperature, operating in the ω–θ scan mode (scan width 1.2°, scan speed 0.03° s^{-1}) with 10 s background counts at each end of the scan range.

Crystal data. $C_{32}H_{35}ClN_3RhS$, $M = 632.1$, Triclinic, space group $P\bar{1}$, $a = 9.339(2)$, $b = 12.130(3)$, $c = 13.950(3)$ Å, $\alpha = 95.7(1)$, $\beta = 96.3(1)$, $\gamma = 103.9(1)°$, $U = 1\,511.8$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}, $F(000) = 652$, μ(Mo-K_α) = 6.7 cm^{-1}.

Of 5 326 independent reflections in the range $3 < 2\theta < 50°$, 3 225 having $I \geqslant 2\sigma(I)$ were considered as observed and used for the structure determination and refinement. The standard deviation $\sigma(I)$ was calculated from counting statistics. Two standard reflections were measured every 120 min to check the stability of the crystal and the electronics. Intensities were corrected for Lorentz and polarization effects and put on an absolute scale by Wilson's method; absorption corrections were not applied.

The structure was solved by conventional Patterson and Fourier syntheses. The refinement of the structural model was by the method of full-matrix least squares, with anisotropic thermal parameters for the Rh, Cl, S, N, and the carbon atoms except those belonging to the phenyl ring which were refined as a rigid group and restricted to their normal geometry (D_{6h} symmetry, C–C 1.395 Å). Hydrogen-atom contributions were fixed (C–H 1.02 Å, $B_{iso} = 7$ Å^2). The final difference-Fourier synthesis was practically featureless.

Mean values of $w\Delta^2$ showed virtually no dependence on $h^{-1}\sin\theta$ and $|F_o|$. Convergence was achieved at $R = (\Sigma|F_o| - |F_c|)/\Sigma F_o = 0.046$ and $R' = |\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2|^{\frac{1}{2}} = 0.046$. The function minimized was $\Sigma w\Delta^2$ in which $w = 1.9390/(\sigma^2|F_o| + 0.000\,345\,|F_o|^2)$ and $\Delta = |F_o| - |F_c|$.

Atomic scattering factors were taken from ref. 30. Allowance was made for the anomalous scattering of rhodium, chlorine, and sulphur, using values of $\Delta f'$ and $\Delta f''$ from ref. 17. All the calculations were performed with the SHELX 76 set of programs [31] on the IBM 4341 computer of the Centro di Calcolo, University of Messina.

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