Binuclear Diaryltriazenido- and Aryl(1-aryliminoethyl)amido-complexes of Rhodium †

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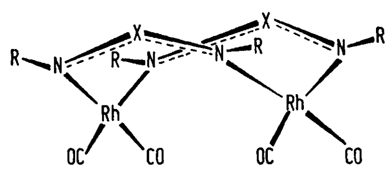
The complex [{RhCl(CO)$_2$}$_2$] reacts with Na[RNNNR] (R = C_6H_4Me-*p*) or Li[RNC(Me)NR] (R = Ph or C_6H_4Me-*p*) to give [{Rh(μ-L)(CO)$_2$}$_2$] [L = RNNNR (1) or RNC(Me)NR (2)]. Complexes (1) and (2) undergo substitution reactions with PPh$_3$, to yield [{Rh(RNNNR)(CO)(PPh$_3$)}$_2$] (3; R = C_6H_4Me-*p*) and [Rh$_2${RNC(Me)NR}$_2$(CO)$_3$(PPh$_3$)] (4; R = Ph) respectively, and oxidative addition with I$_2$ yielding [{RhI(μ-L)(CO)$_2$}$_2$] (5). With cyclo-octa-1,5-diene (cod) or norbornadiene (nbd), (1) affords [Rh$_2$(RNNNR)$_2$(CO)$_2$(cod)] (6) and [{Rh(RNNNR)(diene)}$_n$] (7; diene = cod or nbd).

In a continuation of our studies[1] of the reactivity of complexes of the triazenido-, [RNNNR]$^-$, and 1-iminoethylamido-, [RNC(Me)NR]$^-$ ligands we have turned our attention to species in which such ligands bridge two metals. Although [{Rh(RNNNR)(CO)$_2$}$_2$] (R = Ph or C_6H_4F-*p*) was first prepared in 1973,[2] by the high-pressure carbonylation of [{Rh(RNNNR)(cod)}$_2$] (cod = cyclo-octa-1,5-diene), its reactions were not studied. In order to investigate the effect of bridge-splitting reagents on binuclear triazenido- and 1-iminoethylamido-bridged complexes we have prepared [{Rh(μ-L)(CO)$_2$}$_2$] [L = RNNNR or RNC(Me)NR (R = aryl)] and compared, where possible, their reactions with phosphine ligands, iodine, and cyclic polyolefins. In addition, comparisons are made with the chemistry of known ligand-bridged analogues such as [{Rh(μ-L)(CO)$_2$}$_2$] (L = Cl, O$_2$CMe, or SR).

Results and Discussion

The reaction of Na[RNNNR] (R = C_6H_4Me-*p*) in tetrahydrofuran (thf), or Li[RNC(Me)NR] (R = Ph or C_6H_4Me-*p*) in diethyl ether with [{RhCl(CO)$_2$}$_2$] results in the isolation in good yields of red crystalline [{Rh(μ-L)(CO)$_2$}$_2$] [L = RNNNR (1) or L = RNC(Me)-NR (2)] (Tables 1 and 2). Mass spectroscopy not only verifies the dimeric nature of (1) and (2) but also that the sequential loss of four carbonyl ligands is the first step in the fragmentation process. The i.r. spectra of (1) and (2) in the carbonyl region show, in each case, three absorptions (Table 1) in accord with the C_{2v} symmetry of the proposed structure. A similar struc-



(1) X = N
(2) X = CMe

ture has been found for the closely related allylpalladium complex [{Pd(MeNNNMe)(η^3-C_3H_4Me)}$_2$].[3] A comparison of the carbonyl-stretching frequencies of (1) and (2) suggests that the aryl(1-aryliminoethyl)amide ligand is a better σ donor (or worse η acceptor) than the diaryltriazenide-group. Similar relative donor-acceptor properties have been noted[1] for the diarylacetamidine and diaryltriazene ligands.

Complexes (1) and (2) undergo carbonyl-substitution reactions with PPh$_3$ at room temperature in hexane giving [{Rh(RNNNR)(CO)(PPh$_3$)}$_2$] (3; R = C_6H_4Me-*p*) and [Rh$_2${RNC(Me)NR}$_2$(CO)$_3$(PPh$_3$)] (4; R = Ph) respectively (Tables 1 and 2). Complex (3) was also the major product of the reaction between (1) and excess of PPh$_3$ in refluxing ethanol. The isolation from this reaction of only trace amounts of the mononuclear

† No reprints available.

[1] N. G. Connelly and Z. Demidowicz, *J.C.S. Dalton*, 1978, 50.
[2] W. H. Knoth, *Inorg. Chem.*, 1973, **12**, 38.
[3] P. Hendricks, K. Olie, and K. Vrieze, *Crystal Struct. Comm.*, 1975, **4**, 611.

complex [Rh(RNNNR)(CO)$(PPh_3)_2$] [4] is an indication of the inertness of the triazenido-bridge towards cleavage. In contrast, [{Rh(μ-X)$(CO)_2$}$_2$] (X = Cl,[5] O_2CMe,[6] or SR[7]) readily undergoes bridge-splitting reactions at room temperature with excess of phosphine ligands. Attempts to substitute (4) further, under more vigorous conditions, resulted in decomposition.

The observation of two closely spaced carbonyl absorptions in the i.r. spectrum of (3) confirms mono-substitution at each rhodium atom rather than disubstitution at one. There are therefore two possible structures for (3) as shown below. Although (3a) might be expected on steric grounds (3b) cannot be ruled out, particularly since an *X*-ray study [8] has shown that [{Rh(μ-Cl)(CO)(PMe_2Ph)}$_2$] has the *cis* structure in the solid state. It is noteworthy that in solution this complex exists as a mixture of *cis* and *trans* forms whereas there is no spectral evidence for more than one isomer of (3). Monitoring the reaction of (1) with PPh_3 by i.r. spectroscopy shows the formation of an intermediate having two carbonyl absorptions at 2 059 and 1 999 cm^{-1} and one at *ca.* 1 965 cm^{-1}, obscured by the bands due to (3). Although the intermediate could not be isolated its identity as [$Rh_2(RNNNR)_2(CO)_3(PPh_3)$] (R = Ph) follows from the similarity between its carbonyl i.r. spectrum and that of (4) (Table 1). The reactions of (1) with other phosphorus-donor ligands result in inseparable mixtures of mono- and di-substituted binuclear complexes. Triphenyl phosphite and (2) yield a complex having an i.r. carbonyl spectrum similar to that of

TABLE 1

Analytical and mass and i.r. spectroscopic data for binuclear diaryltriazenido- and aryl(1-aryliminoethyl)amido-complexes of rhodium

Complex	R	Yield (%)	M [a,b] (m/e)	Analysis (%) [b] C	H	N	ν(CO) [c]/cm^{-1}
[{Rh(RNNNR)$(CO)_2$}$_2$]	C_6H_4Me-*p*	80	766 (766)	50.3 (50.2)	4.0 (3.7)	11.0 (11.0)	2 087s, 2 058ms, 2 021s [d]
[{Rh[RNC(Me)NR]$(CO)_2$}$_2$]	Ph	60	736 (736)	52.2 (52.2)	3.7 (3.5)	7.4 (7.6)	2 074s, 2 047ms, 2 004s [d]
	C_6H_4Me-*p*	42	792 (792)	54.3 (54.5)	4.4 (4.3)	6.9 (7.0)	2 072s, 2 045ms, 2 003s [e]
[Rh_2{RNC(Me)NR}$_2(CO)_3(PPh_3)$]	Ph	52	970 (970)	59.8 (60.6)	4.4 (4.2)	6.0 (5.8)	2 053s, 1 987s, 1 968 (sh) [e]
[{Rh(RNNNR)(CO)(PPh_3)}$_2$]	C_6H_4Me-*p*	62		64.2 (64.2)	4.9 (4.7)	7.0 (6.8)	1 977s, 1 963s [f]
[{RhI(RNNNR)$(CO)_2$}$_2$]	C_6H_4Me-*p*	38		37.3 (37.7)	2.8 (2.8)	8.3 (8.2)	2 120s, 2 100m, 2 082ms, 2 073 (sh) [d]
[{RhI[RNC(Me)NR]$(CO)_2$}$_2$]	Ph	10		38.4 (38.8)	3.1 (2.6)	5.4 (5.7)	2 112s, 2 090m, 2 078ms, 2 062 (sh) [f]
[$Rh_2(RNNNR)_2(CO)_2$(cod)]	C_6H_4Me-*p*	6	818 (818)	55.9 (55.8)	5.4 (4.9)	10.2 (10.3)	2 064s, 2 002s [f]
[{Rh(RNNNR)(cod)}$_n$]	C_6H_4Me-*p*	65	435 (435) [g]	60.8 (60.7)	6.3 (6.0)	9.5 (9.7)	
[{Rh(RNNNR)(nbd)}$_n$]	C_6H_4Me-*p*	73	419 (419) [g]	59.8 (60.2)	5.4 (5.3)	9.9 (10.0)	

[a] Determined by mass spectroscopy. [b] Calculated values are given in parentheses. [c] s = Strong, m = medium, w = weak, br = broad, and sh = shoulder. [d] In CCl_4. [e] In hexane. [f] In CH_2Cl_2. [g] Value calculated for $n = 1$.

TABLE 2

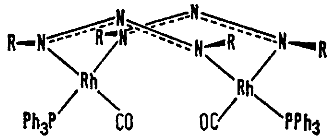
Hydrogen-1 n.m.r. data for binuclear diaryltriazenido- and aryl(1-aryliminoethyl)amido-complexes of rhodium

Complex	R	τ (in $CDCl_3$) [a]
[{Rh(RNNNR)$(CO)_2$}$_2$]	C_6H_4Me-*p*	2.50 (8 H, d, $\lvert J_o + J_p \rvert$ 8, *o*-C_6H_4), 3.00 (8 H, d, $\lvert J_o + J_p \rvert$ 8, *m*-C_6H_4), 7.72 (12 H, s, C_6H_4*Me-p*)
[{Rh[RNC(Me)NR]$(CO)_2$}$_2$]	Ph	2.90 (20 H, m, Ph), 8.30 (6 H, s, CMe) [b]
	C_6H_4Me-*p*	2.97 (8 H, d, $\lvert J_o + J_p \rvert$ 8, *o*-C_6H_4), 3.23 (8 H, d, $\lvert J_o + J_p \rvert$ 8, *m*-C_6H_4), 7.65 (12 H, s, C_6H_4*Me-p*), 8.33 (6 H, s, CMe) [b]
[Rh_2{RNC(Me)NR}$_2(CO)_3(PPh_3)$]	Ph	3.00 (35 H, m, PPh_3 and Ph), 8.28 (3 H, s, CMe), 8.50 (3 H, s, CMe)
[{Rh(RNNNR)(CO)(PPh_3)}$_2$]	C_6H_4Me-*p*	2.87 (46 H, m, PPh_3 and C_6H_4), 7.67 (6 H, s, C_6H_4*Me-p*), 7.90 (6 H, s, C_6H_4*Me-p*)
[{RhI(RNNNR)$(CO)_2$}$_2$]	C_6H_4Me-*p*	2.94 (16 H, s, C_6H_4), 7.62 (12 H, s, C_6H_4*Me-p*)
[$Rh_2(RNNNR)_2(CO)_2$(cod)]	C_6H_4Me-*p*	2.70 (16 H, m, C_6H_4), 5.80 (4 H, br m, olefinic C_8H_{12}), 7.44 (4 H, br m, saturated C_8H_{12}), 7.66 (6 H, s, C_6H_4*Me-p*), 7.74 (6 H, s, C_6H_4*Me-p*), 8.10 (4 H, br m, saturated C_8H_{12})
[{Rh(RNNNR)(cod)}$_n$]	C_6H_4Me-*p*	2.98 (4 H, d, $\lvert J_o + J_p \rvert$ 8, *o*-C_6H_4), 3.18 (4 H, d, $\lvert J_o + J_p \rvert$ 8, *m*-C_6H_4), 5.39 (4 H, br m, olefinic C_8H_{12}), 7.55 (4 H, br m, saturated C_8H_{12}), 7.72 (6 H, s, C_6H_4*Me-p*), 8.20 (4 H, br m, saturated C_8H_{12})
[{Rh(RNNNR)(nbd)}$_n$]	C_6H_4Me-*p*	2.72 (4 H, d, $\lvert J_o + J_p \rvert$ 8, *o*-C_6H_4), 2.96 (4 H, d, $\lvert J_o + J_p \rvert$ 8, *m*-C_6H_4), 5.64 (3 H, br m, C_7H_8), 6.05 (3 H, br m, C_7H_8), 7.66 (6 H, s, C_6H_4Me-*p*), 8.60 (2 H, br s, C_7H_8)

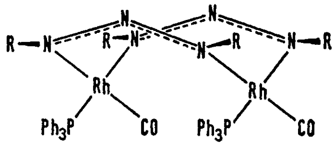
[a] *J* values in Hz. [b] In CCl_4.

[4] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton*, 1974, 1205.
[5] L. Vallarino, *J. Chem. Soc.*, 1957, 2287.
[6] G. Csontos, B. Heil, and L. Marko, *J. Organometallic Chem.*, 1972, **37**, 183.
[7] E. S. Bolton, R. Halvin, and G. R. Knox, *J. Organometallic Chem.*, 1969, **18**, 153.
[8] J. J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat, and R. Poilblanc, *Inorg. Chem.*, 1975, **14**, 743.

(4) but no analytically pure sample could be obtained.

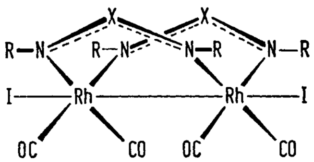


(3a)



(3b)

The addition of 1 equivalent of I_2 to hexane solutions of (1) or (2) gives red-black crystalline adducts for which elemental analysis suggests the formula [{RhI(L)-$(CO)_2$}$_n$] [L = *p*-$MeC_6H_4NNNC_6H_4Me$-*p* (5) or PhNC-(Me)NPh (6)]. Although no mass spectrum could be

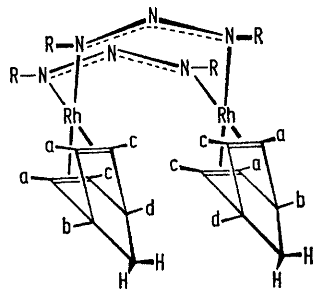


(5) X = N
(6) X = CMe

recorded for either (5) or (6) the solubility of the complexes in non-polar solvents such as CCl_4 or toluene, and ^{1}H n.m.r. and i.r. spectroscopic data, suggests that the complexes are symmetrical, neutral, diamagnetic dimers [{RhI(μ-L)$(CO)_2$}$_2$]. The carbonyl i.r. spectra of (5) and (6) are very similar in pattern to those of (1) and (2) suggesting related basic structures. The average shift of *ca.* 45 cm^{-1} to higher wavenumber of the carbonyl bands of (5) and (6) relative to those of (1) and (2) is consistent with a change in oxidation state from Rh^I to Rh^{III} for both metal atoms. Oxidative addition of I_2 to (1) and (2), with concurrent metal–metal bond formation, to give (5) and (6) with the structure shown is in agreement with the available data, and a similar addition reaction has been reported[9] between I_2 and $[Rh_2(CNR)_4(\mu\text{-}Ph_2PCH_2PPh_2)_2]^{2+}$. The reaction of (5) with 1 equivalent of PPh_3, which results in the immediate regeneration of (1), lends further support to the suggestion that no great structural change occurs on addition of I_2 to (1) or (2).

The reactions of (1) with cyclic polyolefins such as cyclo-octa-1,5-diene (cod), norbornadiene (nbd), cyclo-octatetraene (cot), or cycloheptatriene (cht) result in a variety of products. Prolonged reaction in refluxing n-heptane affords red precipitates which are only partially soluble in solvents such as CH_2Cl_2 and $CHCl_3$. Thus, only with cod and nbd were pure products obtained, having elemental analyses (Table 1) consistent with the formula [{Rh(RNNNR)(olefin)}$_n$] [7; olefin = cod or nbd; R = C_6H_4Me-*p*]. The cod complex has previously been prepared (R = Ph or C_6H_4F-*p*)[2] from Li[RNNNR] and [{Rh(μ-Cl)(cod)}$_2$] and molecular-weight measurements gave $n = 1$ in boiling benzene; some evidence was found for the presence of dimers at 5 °C. Our attempts to determine the value of n for (7) have met with mixed fortune. The highest peak in the mass spectrum of (7) corresponded to that expected for $n = 1$ but molecular-weight determinations in $CHCl_3$ [olefin = nbd, *M* 508 (Calc. for $n = 1$: 419)] or CH_2Cl_2 [olefin = cod, *M* 666 (Calc. for $n = 1$: 435)] suggested $1 < n < 2$. The ^{1}H n.m.r. spectrum (Table 2) of (7; olefin = nbd) does not appear, however, to be consistent with a monomeric structure. Apart from resonances due to the diaryl-triazenide ligand, three broad multiplets are observed at τ 5.64, 6.05, and 8.60 (relative intensity 3 : 3 : 2). The peak at highest field may be assigned to the methylene protons of the nbd ligand, leaving the remaining absorptions due to the olefinic and tertiary protons. The relative intensities of the two peaks can only be explained if the dimeric structure shown below is adopted by (7; diene = nbd). The broad signal at τ 5.64 may then be assigned to protons H_a and H_b and that at τ 6.05 to protons H_c and H_d (alternatively to H_a plus H_d and to H_b plus H_c).

A value of $n = 2$ for (7) would not be unreasonable



(7)

since the closely related complexes [{Rh(O_2CMe)-(cod)}$_2$][10] and [{Rh(μ-SR)(diene)}$_2$] (diene = cod or cot)[11] are both dimeric. In addition we have noted above the relative inertness to cleavage of the triazenide bridge in the reactions of (1) with PPh_3 and I_2.

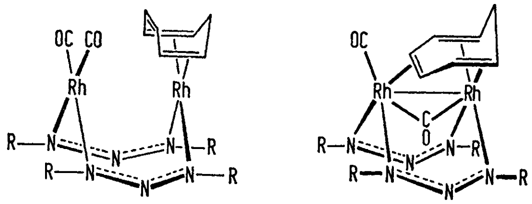
Monitoring, by i.r. spectroscopy, of the reaction between (1) and cyclic polyolefins in refluxing n-heptane reveals the formation of carbonyl-containing intermediates. In the case of cod, curtailment of the reaction when the concentration of the intermediate was maximised, evaporation to dryness of the reaction mixture, and column chromatography allowed the isolation of red crystalline $[Rh_2(RNNNR)_2(CO)_2(olefin)]$ (8; olefin = cod) (Tables 1 and 2). The nbd and cot analogues could not be prepared. A similar intermediate has been isolated from the reaction between cot and

[9] A. L. Balch, *J. Amer. Chem. Soc.*, 1976, **98**, 8049.
[10] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1957, 4735.
[11] R. Hill, B. A. Kelly, F. G. Kennedy, S. A. R. Knox, and P. Woodward, *J.C.S. Chem. Comm.*, 1977, 434.

[{Rh(μ-SPh)(CO)$_2$}$_2$], and structurally characterised.[11] In contrast to [Rh_2(μ-SPh)$_2$(CO)$_2$(cot)], (8; olefin = cod) is not fluxional between −90 and 60 °C. The chelation of the diene to one rhodium atom in (8) contrasts with the monosubstitution of each metal in (3); the i.r. carbonyl spectra (Table 1) of the two complexes clearly reflect the structural difference.

The isolation of (8; olefin = cod) suggested a means by which the value of *n* could be unequivocally established for (7). However, the reaction of (8) with nbd gave only (7; olefin = nbd) rather than the mixed-olefin complex [Rh_2(RNNNR)$_2$(cod)(nbd)] (R = C_6H_4-Me-*p*).

The reaction of (1) with excess of cht in refluxing n-heptane affords a blue-black microcrystalline complex (9), deposited from the reaction mixture, *via* the intermediate [8; olefin = cht, ν(CO) in n-heptane at 2 064 and 2 004 cm^{-1}]. In Nujol the i.r. spectrum of (9) shows one terminal carbonyl band at 1 965 cm^{-1} and a peak at 1 804 cm^{-1} assignable to a bridging carbonyl. On attempted purification, by extraction into boiling $CHCl_3$, only brown materials showing carbonyl bands at 2 087 and 2 018 cm^{-1} could be recovered. Although, therefore, no further characterisation of (9) could be carried out, a structure (b) can be tentatively suggested.



(a) (b)

The formation of (9) from (8; olefin = cht), structure (a), by co-ordination of the free olefinic bond is possible.

EXPERIMENTAL

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. The compounds [{RhCl(CO)$_2$}$_2$],[12] RNNNHR (R = C_6H_4Me-*p*),[13] and RNC(Me)NHR (R = Ph or C_6H_4-Me-*p*)[14] were prepared by published procedures. All the solvents were dried and deoxygenated before use.

Infrared spectra were recorded on a Perkin-Elmer PE257 spectrophotometer and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Hydrogen-1 n.m.r. spectra were recorded on Varian Associates HA100 and JEOL JNM-PS-100 spectrometers at 100 MHz using tetramethylsilane as internal reference. Mass spectra were recorded at 70 eV on an A.E.I. MS 902 instrument.* Microanalyses were by the Microanalytical Service of the School of Chemistry, University of Bristol.

*Bis-μ-[di-*p*-tolyltriazenido*(1−)-N^1N^3]-*bis(dicarbonylrhodium)*, [{Rh(*p*-MeC_6H_4NNNC_6H_4Me-*p*)(CO)$_2$}$_2$] (1; R = C_6H_4Me-*p*).—To a solution of Na[*p*-MeC_6H_4NNNC_6H_4Me-*p*] in thf (60 cm^3), prepared from a 50% dispersion (in mineral oil) of NaH (1.50 g) and *p*-MeC_6H_4NNNHC_6H_4Me-*p* (1.15 g, 5.10 mmol), was added [{RhCl(CO)$_2$}$_2$] (1.0 g, 2.60 mmol). After stirring for 24 h the deep red solution was evaporated to dryness. Extraction of the residue into n-hexane (110 cm^3), evaporation to low volume, and cooling to 0 °C gave the *complex* as dark red crystals, yield 1.57 g (80%). The complex is soluble in all the common organic solvents to give deep red solutions which slowly decompose in air.

The *complexes* [Rh_2{RNC(Me)NR}$_2$(CO)$_4$] (2; R = Ph or C_6H_4Me-*p*) were prepared in a similar manner from Li[RNC(Me)NR] and [{RhCl(CO)$_2$}$_2$] in diethyl ether. The lithium salts were preformed *in situ* from the amidine, RNC(Me)NHPh, and butyl-lithium.

Di-μ-[phenyl(1-phenyliminoethyl)amido-NN^1]-*tricarbonyl-(triphenylphosphine)dirhodium*, [Rh_2}PhNC(Me)NPh}$_2$(CO)$_3$-(PPh_3)] (4; R = Ph).—To a solution of (2; R = Ph) (0.37 g, 0.50 mmol) in hexane (50 cm^3) was added PPh_3 (0.27 g, 1.00 mmol). After stirring for 3.5 h the mauve precipitate was collected and recrystallised from tetrahydrofuran–diethyl ether to give the complex as purple *crystals*, yield 0.32 g (52%). The complex is sparingly soluble in hexane but soluble in more polar solvents such as thf and CH_2Cl_2 giving moderately air-stable solutions.

*Bis-μ-[di-*p*-tolyltriazenido*(1−)-N^1N^3]-*bis[carbonyl(triphenylphosphine)rhodium]*, [{Rh(*p*-MeC_6H_4NNNC_6H_4Me-*p*)-(CO)(PPh_3)}$_2$] (3; R = C_6H_4Me-*p*).—*Method* (*a*). To complex (1; R = C_6H_4Me-*p*) (0.20 g, 0.26 mmol) in hexane (75 cm^3) was added PPh_3 (0.14 g, 0.53 mmol). After stirring for 94 h the resulting orange precipitate was removed, dissolved in the minimum volume of CH_2Cl_2, and chromatographed on an alumina–hexane column. Elution with CH_2Cl_2–hexane (1 : 1) afforded an orange band which was collected. The orange solution was then evaporated to low volume. Cooling to 0 °C gave the complex as red *crystals*, yield 0.20 g (62%).

Method (*b*). Complex (1; R = C_6H_4Me-*p*) (0.14 g, 0.18 mmol) and PPh_3 (0.20 g, 0.76 mmol) were heated under reflux in ethanol (20 cm^3) for 17 h. Cooling to room temperature gave the complex as red *crystals*, yield 0.15 g (66%).

The complex is insoluble in hexane or ethanol but soluble in CH_2Cl_2 to give a moderately air-stable solution.

*Bis-μ-[di-*p*-tolyltriazenido*(1−)-N^1N^3]-*bis(dicarbonyliodorhodium)*, [{RhI(*p*-MeC_6H_4NNNC_6H_4Me-*p*)(CO)$_2$}$_2$] (5; R = C_6H_4Me-*p*).—To a solution of (1; R = C_6H_4Me-*p*) (0.10 g, 0.13 mmol) in hexane (50 cm^3) was added I_2 (0.033 g, 0.13 mmol). After stirring for 10 min the red-black solution was filtered, evaporated to low volume, and cooled to 0 °C to give the complex as black *crystals*, yield 0.05 g (38%).

Using the same method, [{RhI[PhNC(Me)NPh](CO)$_2$}$_2$] (6; R = Ph) was precipitated from the reaction mixture. It may be recrystallised from thf–hexane as black crystals.

*Dicarbonyl(cyclo-octa-1,5-diene)-bis-μ-[di-*p*-tolyltriazenido*(1−)-N^1N^3]-*dirhodium*, [Rh_2(*p*-MeC_6H_4NNNC_6H_4Me-*p*)$_2$(CO)$_2$(cod)].—A mixture of (1; R = C_6H_4Me-*p*) (0.50 g, 0.65 mmol) and cod (0.5 cm^3) was heated gently under reflux for 44 h in n-heptane (100 cm^3). After cooling to room temperature the mixture was filtered and evaporated to low volume. Crystallisation at 0 °C gave 0.39 g of the crude product which was dissolved in the minimum volume

* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[12] J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1966, **8**, 211.

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of toluene and chromatographed on an alumina–hexane column. Elution with hexane gave an orange band which was removed from the column. Reduction of the resulting orange solution to low volume and cooling to 0 °C gave the complex as dark red *crystals*, yield 0.03 g (6%). The complex is soluble in common organic solvents giving red solutions which slowly decompose in air.

*Bis-μ-[di-*p*-tolyltriazenido*(1−)-N^1N^3]-*bis*[(*η-cyclo-octa-1,5-diene*)*rhodium*], [{Rh(*p*-$MeC_6H_4NNNC_6H_4Me$-*p*)(cod)}$_2$] (7; R = C_6H_4Me-*p*).—A mixture of (1; R = C_6H_4Me-*p*) (0.30 g, 0.39 mmol) and cod (0.5 cm^3) was heated under reflux in n-heptane (60 cm^3) for 51 h. On cooling to room temperature the precipitate was removed and washed well with ethanol to give the product as a red *solid*, yield 0.22 g (65%). The complex [{Rh(*p*-$MeC_6H_4NNNC_6H_4Me$-*p*)-(nbd)}$_2$] (nbd = norbornadiene) was prepared similarly. The complexes are only moderately soluble in polar solvents such as CH_2Cl_2 and $CHCl_3$.

Z. D. thanks the S.R.C. for the award of a Studentship.

[8/097 *Received*, 19*th January*, 1978]