1H-Pyrrolo[2,3-b]pyridine (HL) Ligands in Rhodium(I) and Iridium(I) Chemistry. Crystal and Molecular Structures of [Rh₂(μ-L)₂(nbd)₂] and [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂(CO)₂(nbd)₂]†

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Reactions of 1H-pyrrolo[2,3-b]pyridine (HL) with [Rh(diolefin)₂][ClO₄] or [Rh₂Cl₂(diolefin)₂] compounds give mononuclear [Rh(diolefin)(HL)₂][ClO₄] or [RhCl(diolefin)(HL)] complexes respectively. The latter react with KOH to form binuclear [Rh₂(μ-L)₂(diolefin)₂] complexes. Carbonylation reactions of the above compounds afford [Rh(CO)₂(HL)₂][ClO₄], [RhCl(CO)₂(HL)], or [Rh₂(μ-L)₂(CO)₄]. Some related iridium(I) complexes are also reported. Redistribution reactions take place between [Rh₂(μ-L)₂(diolefin)₂] and [Rh₂(μ-L)₂(CO)₄] yielding [(diolefin)Rh(μ-L)₂-Rh(CO)₂] complexes. The tetranuclear complex [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂(CO)₂(nbd)₂] has been isolated by several routes starting from the above mono- or bi-nuclear neutral rhodium complexes. The structures of the complexes [Rh₂(μ-L)₂(nbd)₂] and [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂-(CO)₂(nbd)₂] (nbd = norborna-2,5-diene) have been determined by X-ray methods. The former crystallizes in the monoclinic space group C2/c with a = 16.272(4), b = 7.932(2), c = 19.198(5) Å, β = 112.07(2)°, and Z = 4. Crystals of the latter are monoclinic, space group P2₁/n with Z = 2 and a unit cell of dimensions a = 11.091(3), b = 16.615(6), c = 8.531(4) Å, and β = 91.63(3)°. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares to R values of 0.072 and 0.041 respectively. The structure of the binuclear complex consists of two Rh atoms bridged by two anions L co-ordinated through the two N atoms. Each Rh atom interacts also with the olefinic bonds of a nbd molecule. The ligand L is disordered and distributed in two positions. The structure of the tetranuclear complex consists of two binuclear units joined together through a double chlorine bridge, forming a planar Rh₄Cl₂ ring. In each binuclear unit a bidentate anion L and a carbonyl group bridge the two Rh atoms, which are directly bonded [Rh–Rh 2.686(2) Å].

Considerable interest has recently been shown in binuclear complexes containing rhodium(I) centres in close proximity.[1] Among those, complexes with binucleating ligands containing P–C–P or P–C–N bridging units [e.g. bis(diphenylphosphino)-methane[2] or 2-(diphenylphosphino)pyridine[3]] have been studied. In this context we have already reported some binuclear rhodium complexes with 1,8-naphthyridine (A)[4] and 1,8-naphthyridin-2-one (B)[5] ligands, that like bis(diphenylphosphino)methane have only a single carbon atom separating the two donor centres.

We report now the chemical and co-ordinative behaviour of 1H-pyrrolo[2,3-b]pyridine (HL) (C), an uncommon ligand that we hoped would be useful for the construction of new bi- or multi-nuclear rhodium complexes. The X-ray structures of the binuclear complex [Rh(μ-L)₂(nbd)₂] and of the tetranuclear [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂(CO)₂(nbd)₂] (nbd = norborna-2,5-diene) have been determined. A preliminary report for the tetra-nuclear complex has been given.[6]

(A)   (B)   (C)
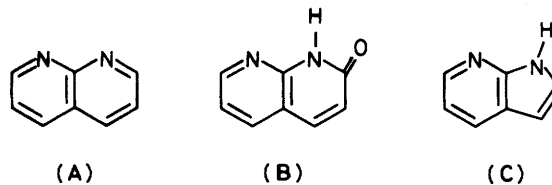
Results and Discussion

Mononuclear Complexes.—Addition of HL to dichloro-methane solutions of compounds of the type [M₂Cl₂-(diolefin)₂] gives rise to yellow air-stable complexes of formula [MCl(diolefin)(HL)] {M = Rh, diolefin = cyclo-octa-1,5-diene (cod) (1), nbd (2), tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene (tfbb) (3), or 1,3,8-trimethyl(tetrafluorobenzo[5,6])-bicyclo[2.2.2]octa-2,5,7-triene (Me₃tfbb) (4); M = Ir, diolefin = (cod) (5)}. These complexes are non-electrolytes in acetone and their molecular weights (Table 1), in solution, correspond to mononuclear species. Bubbling of carbon monoxide through dichloromethane solutions of the compounds (1)—(5) leads to the formation of [MCl(CO)₂(HL)] complexes [M = Rh (6) or Ir (7)] which exhibit two ν(CO) bands in the 2 100—2 000 cm⁻¹ region, characteristic of cis-dicarbonylmetal complexes. Complex (6) can alternatively be obtained by reaction of [Rh₂Cl₂(CO)₄] with HL in dichloromethane. Attempts to prepare [RhCl(CO)(HL)(PPh₃)] by reaction of a stoicheio-metric amount of PPh₃ with complex (6) results in the formation of [RhCl(CO)(PPh₃)₂] as the main product.

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† Bis{μ-1H-pyrrolo[2,3-b]pyridinato(1 –)-N¹N⁷}-bis[(η-norborna-2,5-diene)rhodium] and di-μ-chloro-bis[μ-carbonyl-1-carbonyl-2-(η-norborna-2′,5′-diene)-μ-{1H-pyrrolo[2,3-b]pyridinato(1 –)-N¹(Rh¹)-N⁷(Rh²)}-dirhodium(Rh–Rh)].

Supplementary data available (No. SUP 56261, 6 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structures factors are available from the editorial office.

Table 1. Colours, analytical and physical data for the new complexes

Compound	Colour	Yield (%)	Analysis (%)[a] C	H	N	M^b	I.r. bands (cm⁻¹)
(1) [RhCl(cod)(HL)]	Yellow	85	49.2 (49.4)	5.30) (4.95)	7.70 (7.70)	336 (365)	
(2) [RhCl(nbd)(HL)]	Yellow	85	48.2 (48.2)	4.50 (4.05)	7.95 (8.00)	362 (349)	
(3) [RhCl(tfbb)(HL)]	Yellow	75	46.8 (47.3)	2.80 (2.50)	5.65 (5.80)		
(4) [RhCl(Me₃tfbb)(HL)]	Yellow	70	50.1 (50.35)	3.50 (3.45)	5.50 (5.35)		
(5) [IrCl(cod)(HL)]	Yellow	80	39.5 (39.7)	3.90 (4.00)	5.90 (6.15)		
(6) [RhCl(CO)₂(HL)]	Yellow	80	34.6 (34.6)	1.80 (1.95)	8.95 (8.95)	356 (312)	2 075s, 2 010s (Nujol) 2 085s, 2 015s (CH₂Cl₂) v(CO)
(7) [IrCl(CO)₂(HL)]	Orange	75	27.3 (26.9)	1.85 (1.50)	7.20 (6.95)	435 (401)	2 060s 1 990s (Nujol) 2 080s, 1 995s (CH₂Cl₂) v(CO)
(8) [Rh(cod)(HL)₂][ClO₄]	Yellow	80	47.9 (48.3)	4.70 (4.40)	10.2 (10.25)		1 120s, 1 095s, 1 040s, 625s, 620s v(ClO)
(9) [Rh(nbd)(HL)₂][ClO₄]	Yellow	85	47.25 (47.5)	3.45 (3.80)	10.7 (10.55)		1 140s, 1 095s, 1 040s, 625s, 620s v(ClO)
(10) [Rh(tfbb)(HL)₂][ClO₄]	Yellow	85	46.5 (46.95)	3.30 (2.70)	8.70 (8.45)		1 135s, 1 115s, 1 060s, 620br v(ClO)
(11) [Rh(CO)₂(HL)₂][ClO₄]	White	80	38.75 (38.85)	2.45 (2.45)	11.5 (11.3)		1 185s, 1 150s, 1 115s, 620br v(ClO) 2 100s, 2 040s (Nujol), 2 100s, 2 040s (CH₂Cl₂) v(CO)
(12) [Rh₂(μ-L)₂(cod)₂]	Orange	90	54.5 (54.9)	5.30 (5.20)	8.45 (8.55)	648 (656)	
(13) [Rh₂(μ-L)₂(nbd)₂]	Red	90	53.95 (53.85)	4.35 (4.20)	8.80 (8.95)	604 (624)	
(14) [Rh₂(μ-L)₂(tfbb)₂]	Orange	85	50.5 (51.15)	2.40 (2.50)	6.40 (6.30)	960 (892)	
(15) [Ir₂(μ-L)₂(cod)₂]	Dark red	75	43.4 (43.15)	4.60 (4.10)	6.90 (6.70)	829 (835)	
(16) [Rh₂(μ-L)₂(CO)₄]	Red	70	38.5 (39.15)	2.10 (1.80)	10.15 (10.15)	556 (552)	2 090vs, 2 060s, 2 025vs (Nujol) 2 090vs, 2 065s, 2 020vs (CH₂Cl₂) v(CO)
(17) [Rh₂(μ-L)₂(CO)₂(PPh₃)₂]	Orange	70	61.25 (60.85)	4.10 (4.50)	5.20 (5.45)	1 051 (1 020)	1 965s (Nujol), 1 970 (CH₂Cl₂) v(CO)
(18) [(nbd)Rh(μ-L)₂Rh(CO)₂]	Red	65	46.7 (46.95)	3.10 (3.10)	9.90 (9.50)	591 (588)	2 065s, 2 000s (Nujol) 2 060s, 2 010s (CH₂Cl₂) v(CO)
(19) [(cod)Rh(μ-L)₂Rh(CO)₂]	Orange	50	47.9 (47.7)	3.60 (3.65)	9.40 (9.25)	638 (604)	2 065s, 1 995s, 1 960w (Nujol) 2 065s, 1 995s (CH₂Cl₂) v(CO)
(20) [(tfbb)Rh(μ-L)₂Rh(CO)₂]	Red	70	46.3 (46.55)	2.40 (2.25)	7.65 (7.75)	746 (722)	2 070s, 2 005s, 1 975w (Nujol) 2 070s, 2 005s (CH₂Cl₂) v(CO)
(21) [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂(CO)₂(nbd)₂]	Orange	85	37.85 (37.95)	2.45 (2.60)	5.40 (5.55)	526 (1 012)	2 060w, 2 015s, 1 957w, 1 840s, 1 797w (Nujol) 2 095s, 2 080w, 2 070w, 2 025s (CH₂Cl₂) v(CO)

[a] Required values are given in parentheses. [b] In chloroform. Required values are given in parentheses.

Cationic complexes of the type [Rh(diolefin)(HL)₂][ClO₄] [diolefin = cod (8), nbd (9), or tfbb (10)] are easily obtained by reaction of HL with the corresponding complex [Rh(diolefin)₂]-[ClO₄] in dichloromethane. Carbon monoxide slowly displaces the molecule of co-ordinated diolefin in complexes (8)—(10) to give the related compound [Rh(CO)₂(HL)₂][ClO₄] (11), which shows two v(CO) bands in the 2 100—2 000 cm⁻¹ region, characteristic of cis-dicarbonylrhodium(ı) complexes.[4] The cationic complexes (8)—(11) behave as 1:1 electrolytes in acetone and consequently they show the absorptions expected for the perchlorate anion $(T_d)^7$ in dichloromethane solution at 1 090 and 620 cm⁻¹, but in the solid state these bands are split (see Table 1). The observed splitting could arise from an interaction NH ··· OClO₃ as described for the complex [Rh-(H₂bbzim)(CO)₂][ClO₄]⁸ (H₂bbzim = 2,2′-bibenzimidazole).

In the above mentioned mononuclear complexes the HL ligand is most likely unidentate and co-ordinated to the rhodium through the pyridine nitrogen atom as found in the complex [Rh₂(μ-O₂CC₂H₅)₄(HL)₂].⁹ A broad v(N–H) band in the 3 300—3 170 cm⁻¹ region is observed for these mononuclear derivatives.

Polynuclear Complexes.—Binuclear derivatives. Interestingly the pyrrole NH proton of the co-ordinated HL ligand in the compounds [MCl(diolefin)(HL)] or [RhCl(CO)₂(HL)] can be removed by reaction with potassium hydroxide in methanol to give binuclear complexes of the formula [M₂(μ-L)₂(diolefin)₂] [M = Rh, diolefin = cod (12), nbd (13), or tfbb (14); M = Ir, diolefin = cod (15)] or [Rh₂(μ-L)₂(CO)₄] (16). Complexes (12)—(14) are obtained pure and in higher yield by addition of solid [Rh₂Cl₂(diolefin)₂] complexes to solutions of the anion L (prepared *in situ* by treatment of HL with potassium hydroxide in methanol). An alternative and more convenient method to isolate complex (16) involves the reaction of [Rh(acac)(CO)₂] (acac = acetylacetonate) with HL in methanol. Complex (16) undergoes carbonyl substitution with triphenylphosphine at room temperature in dichloromethane to give [Rh₂(μ-L)₂-(CO)₂(PPh₃)₂] (17). Complex (16) exhibits three strong v(CO)

bands (Table 1) in accord with the C_{2v} symmetry[5] of the proposed structure. A single and broad $v(CO)$ band is observed in the i.r. spectrum of complex (17) suggesting a formula *trans*-[(Ph₃P)(OC)Rh(μ-L)₂Rh(CO)(PPh₃)]. Molecular-weight measurements on complexes (12)—(17) support a binuclear formulation, confirmed by the determination of the structure of complex (13) by *X*-ray methods.

Protonation of [Rh₂(μ-L)₂(cod)₂] with hydrochloric acid in acetone results in bridge cleavage, regenerating the mononuclear complex [RhCl(cod)(HL)].

It is noteworthy that binuclear unsymmetrical complexes [(diolefin)Rh(μ-L)₂Rh(CO)₂] (18)—(20) are obtained by reaction of (12)—(14) with an equimolecular amount of complex (16) in methanol according to equation (1). The

$$[Rh_2(\mu\text{-L})_2(\text{diolefin})_2] + [Rh_2(\mu\text{-L})_2(CO)_4] \rightleftharpoons$$
$$2 [(\text{diolefin})Rh(\mu\text{-L})_2Rh(CO)_2] \quad (1)$$
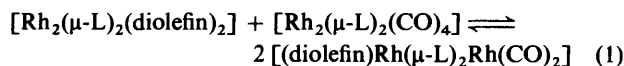
equilibrium (1) must lie far to the right, *i.e.* in favour of the mixed diolefin–carbonyl complex, since only two strong $v(CO)$ bands characteristic of a *cis*-dicarbonylrhodium arrangement are observed in the i.r. spectra in solution and in the solid state (Table 1). Furthermore, complexes (18)—(20) are obtained as pure crystalline solids after evaporation of their solutions.

Tetranuclear complex. The reaction of either complex (13) with [Rh₂Cl₂(CO)₄] or complex (16) with [Rh₂Cl₂(nbd)₂] in methanol at room temperature leads to the formation of an orange solid for which molecular-weight measurements, analytical and spectroscopic data suggest an unsymmetrically bridged complex of formula [{(nbd)Rh(μ-L)(μ-CO)RhCl(CO)}ₓ] (21). This compound is also easily prepared by treatment of complex (2) with [Rh(acac)(CO)₂] or alternatively by reaction of complex (6) with [Rh(acac)(nbd)] (see Scheme). Our attempts to isolate complexes similar to (21) containing other different olefins by the mentioned routes have been unsuccessful. So, a redistribution occurs in the reaction of [Rh₂(μ-L)₂(cod)₂] with [Rh₂Cl₂(CO)₄] to give [Rh₂(μ-L)₂(CO)₄], or [Rh(acac)(CO)₂] is obtained by treating [Rh(acac)(tfbb)] with [RhCl(CO)₂-(HL)].

The i.r. spectrum of complex (21) shows the presence of bridging and terminal carbonyl groups in the solid state, but the structure is not retained in solution since only terminal $v(CO)$ bands are observed in dichloromethane (see Table 1). Furthermore, molecular-weight measurements in dilute chloroform solutions suggest a binuclear formulation. Electron counting for the proposed binuclear unit suggests the presence of a metal–metal bond bridged by a single L anion and a carbonyl group. In the solid state the crystal structure of (21) (see below) reveals an unusual, tetranuclear complex in which two chlorine atoms asymmetrically bridge two binuclear units.

Complex (21) reacts with Na[BH₄] in methanol to give metallic rhodium, whereas it reacts with hydrochloric acid to give an orange solution which on passage through alumina gives the red binuclear complex (18). Attempts to cleave the chloro-bridges in complex (21) by reaction with triphenylphosphine gave [RhCl(CO)(PPh₃)₂] as one of the products.
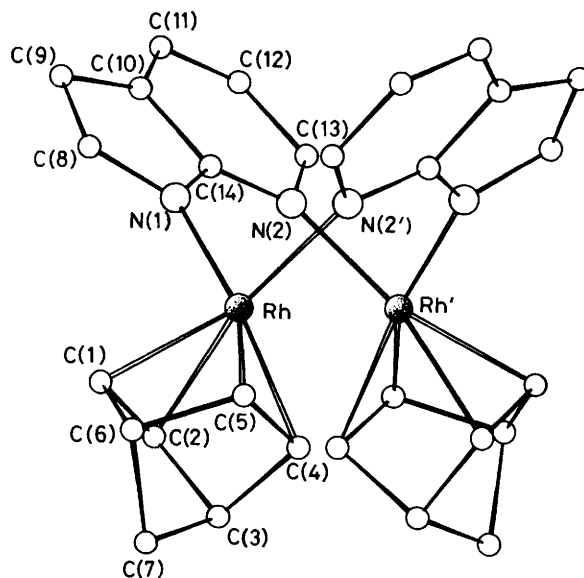
Figure 1. View of the complex [Rh₂(μ-L)₂(nbd)₂] with the atomic numbering scheme
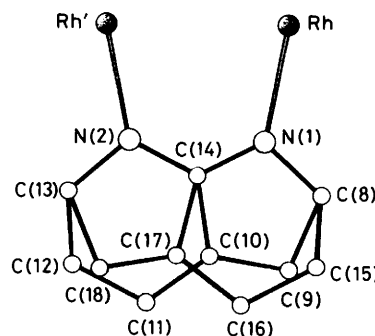
Figure 2. The disordered ligand L, distributed in two positions, in the complex [Rh₂(μ-L)₂(nbd)₂]

Crystal Structures.—(*a*) *Complex* [Rh₂(μ-L)₂(nbd)₂] (13). The structure of the binuclear complex (13) consists of two Rh atoms bridged by two anions L co-ordinated through the two nitrogen atoms. Each Rh atom completes its co-ordination by a nbd molecule interacting through the two double bonds. The complex contains two RhL(nbd) moieties related by a crystallographically imposed two-fold axis. A view of the complex with the atomic numbering scheme is given in Figure 1. Selected bond distances and angles are given in Table 2.

The ligand L is disordered and distributed in two positions (with occupancy factors 0.6 and 0.4 respectively) as the pyrrole and pyridine nitrogen atoms in each ligand can be interchanged
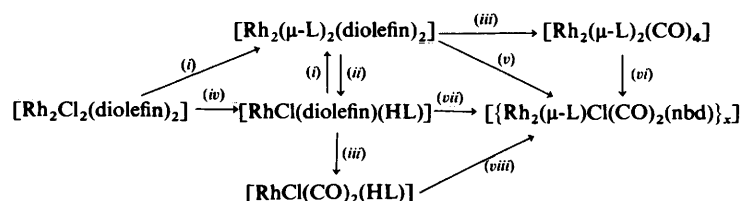
Scheme. (*i*) + HL + KOH(MeOH); (*ii*) + HCl(aq); (*iii*) + CO; (*iv*) + HL; (*v*) + [Rh₂Cl₂(CO)₄]; (*vi*) + [Rh₂Cl₂(nbd)₂]; (*vii*) + [Rh(acac)(CO)₂]
x = 2 in the solid state, 1 in solution; (*viii*) + [Rh(acac)(nbd)]

Table 2. Selected bond distances (Å) and angles (°) for the complex [Rh₂(μ-L)₂(nbd)₂] (13)*

(a) Around the Rh atom

Rh–N(1)	2.111(8)	Rh–C(2)	2.124(10)
Rh–N(2')	2.092(7)	Rh–C(4)	2.157(10)
Rh–C(1)	2.108(9)	Rh–C(5)	2.112(12)

N(1)–Rh–N(2')	90.3(3)	N(2')–Rh–C(5)	93.9(4)
N(1)–Rh–C(1)	95.6(4)	C(1)–Rh–C(2)	38.3(4)
N(1)–Rh–C(2)	99.9(4)	C(1)–Rh–C(4)	80.6(4)
N(1)–Rh–C(4)	163.3(4)	C(1)–Rh–C(5)	68.0(4)
N(1)–Rh–C(5)	153.7(4)	C(2)–Rh–C(4)	67.0(4)
N(2')–Rh–C(1)	148.2(4)	C(2)–Rh–C(5)	80.1(4)
N(2')–Rh–C(2)	167.6(4)	C(4)–Rh–C(5)	38.2(4)
N(2')–Rh–C(4)	101.6(4)		

(b) In the ligand nbd

C(1)–C(2)	1.388(14)	C(3)–C(7)	1.559(13)
C(1)–C(6)	1.548(17)	C(4)–C(5)	1.396(15)
C(2)–C(3)	1.538(16)	C(5)–C(6)	1.558(13)
C(3)–C(4)	1.563(16)	C(6)–C(7)	1.562(14)

C(2)–C(1)–C(6)	106.9(8)	C(4)–C(5)–C(6)	107.5(9)
C(1)–C(2)–C(3)	107.3(9)	C(1)–C(6)–C(5)	98.9(8)
C(2)–C(3)–C(4)	99.3(8)	C(1)–C(6)–C(7)	99.9(8)
C(2)–C(3)–C(7)	100.5(9)	C(5)–C(6)–C(7)	100.4(8)
C(4)–C(3)–C(7)	100.7(9)	C(3)–C(7)–C(6)	94.6(8)
C(3)–C(4)–C(5)	105.9(9)		

(c) In the disordered ligand L

N(1)–C(8)	1.386(11)	N(2)–C(13)	1.404(15)
N(1)–C(14)	1.316(13)	N(2)–C(14)	1.367(10)
C(8)–C(9)	1.44(3)	C(8)–C(15)	1.27(4)
C(9)–C(10)	1.42(3)	C(13)–C(18)	1.48(3)
C(10)–C(11)	1.39(3)	C(14)–C(17)	1.46(3)
C(10)–C(14)	1.44(2)	C(15)–C(16)	1.49(5)
C(11)–C(12)	1.46(3)	C(16)–C(17)	1.44(3)
C(12)–C(13)	1.31(3)	C(17)–C(18)	1.37(4)

Rh–N(1)–C(8)	122(1)	Rh'–N(2)–C(13)	119(1)
Rh–N(1)–C(14)	129(1)	Rh'–N(2)–C(14)	129(1)
C(8)–N(1)–C(14)	110(1)	C(13)–N(2)–C(14)	112(1)
N(1)–C(8)–C(9)	110(2)	N(1)–C(8)–C(15)	129(2)
C(8)–C(9)–C(10)	103(2)	N(2)–C(13)–C(18)	108(2)
C(9)–C(10)–C(11)	134(2)	N(1)–C(14)–C(17)	132(2)
C(9)–C(10)–C(14)	108(2)	N(2)–C(14)–C(17)	103(2)
C(11)–C(10)–C(14)	118(2)	C(8)–C(15)–C(16)	121(3)
C(10)–C(11)–C(12)	117(2)	C(15)–C(16)–C(17)	115(2)
C(11)–C(12)–C(13)	120(2)	C(14)–C(17)–C(16)	113(2)
N(2)–C(13)–C(12)	127(2)	C(14)–C(17)–C(18)	114(2)
N(1)–C(14)–N(2)	125(1)	C(16)–C(17)–C(18)	132(2)
N(1)–C(14)–C(10)	109(1)	C(13)–C(18)–C(17)	102(2)
N(2)–C(14)–C(10)	126(1)		

* Primed atoms are related to the corresponding unprimed ones by a two-fold axis (symmetry equivalent position: $-x$, y, $\frac{1}{2} - z$).

by co-ordination to the metals. The disordered ligand is represented in Figure 2. Each metal is in a slightly distorted square-planar arrangement; if M(1) and M(2) represent the midpoints of the olefinic bonds C(1)–C(2) and C(4)–C(5), the deviations of M(1), M(2), N(1), and N(2') from the best plane passing through them are −0.001(6), 0.001(6), 0.106(7), and −0.109(7) Å respectively, with the Rh atom out of this plane 0.158(2) Å towards the other metal. The deviation of one metal atom from the square co-ordination plane toward the other metal, together with a relatively short Rh–Rh separation, such as 3.167(1) Å,[10] have been considered to indicate some metal–metal interaction in similar binuclear rhodium(I) complexes. In the present case, even if the separation between the Rh atoms is
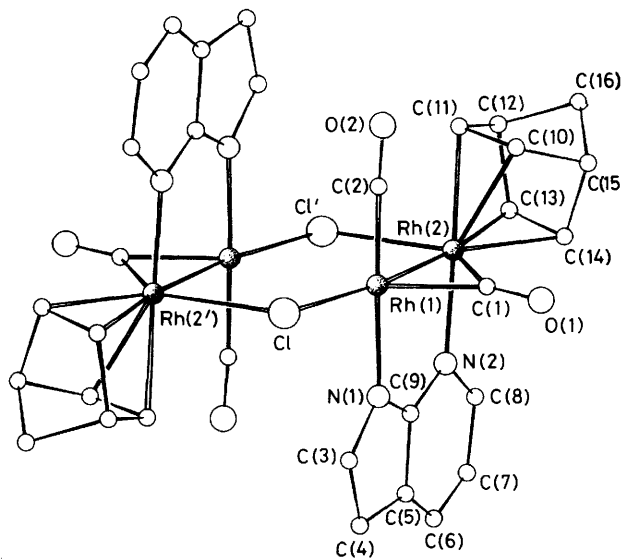
Figure 3. View of the complex [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂(CO)₂(nbd)₂]

rather long [3.207(3) Å], a weak intermetallic interaction cannot be wholly excluded.

The behaviour of the anion L, bonded through its two N atoms to the metals, has already been reported by Cotton *et al.*[11] for the complex [Mo₂(μ-L)₂Cl₂(PEt₃)₂] where the Mo atoms are quadruply bonded, so the present complex is the first case in which this ligand bridges two non-bonded metals. Both disordered ligands are planar with the largest deviations from planarity in each ligand being 0.07(2) and 0.06(3) Å.

The Rh–N bond distances [2.111(8) and 2.092(7) Å] are in the range of those found for closely related complexes with N-donor ligands bridging two rhodium(I) atoms (*e.g.* benz-amidine,[12] naphthyridin-2-one,[5] or naphthyridine[4]), but significantly shorter than that found [2.275(1) Å] for this neutral ligand acting in a unidentate manner in the rhodium(II) complex [Rh₂(O₂CC₂H₅)₄(HL)₂].[9] The two five-membered Rh–N–C–N–Rh' rings are planar; Rh, N(1), C(14), N(2), and Rh' deviate from the mean plane through them by 0.001(1), −0.026(7), −0.018(8), 0.048(7), and −0.001(1) Å respectively. These two planes are nearly perpendicular to one another, the dihedral angle between them being 92.0(1)°. The Rh–C bond distances involving the nbd ligand and the C–C distances and angles within this molecule are quite normal if compared with other complexes with the same ligand.[13] However, the olefinic bonds [1.388(14) and 1.396(15) Å], as expected longer than in the free nbd molecule (1.338 Å),[14] and the Rh–C distance [2.108(9)—2.157(10) Å] are slightly shorter and longer respectively than those found[4] [C–C 1.45(3) and Rh–C 2.09(2)— 2.13(2) Å] for the comparable cationic complex [Rh₂(μ-napy)₂(nbd)₂]²⁺ (napy = naphthyridine) suggesting a weaker diolefin–rhodium bond/interaction for the neutral complex. The carbon atoms [C(1), C(2), C(4), and C(5)] of nbd involved in the co-ordination to the metal are strictly coplanar. This plane forms a dihedral angle of 82.8(3)° with the co-ordination plane of the metal. The planes passing through these carbon atoms in the two ligands form a dihedral angle of 120.6(4)°.

(b) Complex [Rh₄(μ-Cl)₂(μ-L)₂(μ-CO)₂(CO)₂(nbd)₂] (21). A perspective view of the structure of complex (21) is shown in Figure 3, together with the atomic numbering scheme. Selected bond distances and angles are listed in Table 3. The structure consists of a centrosymmetrical tetranuclear complex in which two chlorine atoms asymmetrically bridge [Rh(1)–Cl 2.401(5) and Rh(2)–Cl 2.627(5) Å] two binuclear units in such a way as

Table 3. Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for the complex $[Rh_4(\mu\text{-Cl})_2(\mu\text{-L})_2(\mu\text{-CO})_2(CO)_2(nbd)_2]$ (21)*

(a) Co-ordination sphere of Rh(1)

Rh(1)–Rh(2)	2.686(2)	Rh(1)–C(1)	1.97(2)
Rh(1)–Cl	2.401(5)	Rh(1)–C(2)	1.84(2)
Rh(1)–N(1)	2.088(13)		

Rh(2)–Rh(1)–Cl	167.5(2)	Cl–Rh(1)–C(1)	143.1(5)
Rh(2)–Rh(1)–N(1)	85.9(4)	Cl–Rh(1)–C(2)	89.5(6)
Rh(2)–Rh(1)–C(1)	49.3(5)	N(1)–Rh(1)–C(1)	85.0(6)
Rh(2)–Rh(1)–C(2)	91.2(6)	N(1)–Rh(1)–C(2)	177.1(7)
Cl–Rh(1)–N(1)	93.4(4)	C(1)–Rh(1)–C(2)	93.0(8)

(b) Co-ordination sphere of Rh(2)

Rh(2)–Cl'	2.627(5)	Rh(2)–C(11)	2.20(2)
Rh(2)–N(2)	2.067(14)	Rh(2)–C(13)	2.18(2)
Rh(2)–C(1)	2.05(2)	Rh(2)–C(14)	2.17(2)
Rh(2)–C(10)	2.23(2)		

Rh(1)–Rh(2)–Cl'	88.4(2)	N(2)–Rh(2)–C(10)	153.6(6)
Rh(1)–Rh(2)–N(2)	86.3(4)	N(2)–Rh(2)–C(11)	161.0(6)
Rh(1)–Rh(2)–C(1)	46.8(5)	N(2)–Rh(2)–C(13)	98.7(6)
Rh(1)–Rh(2)–C(10)	101.2(5)	N(2)–Rh(2)–C(14)	94.5(6)
Rh(1)–Rh(2)–C(11)	109.3(5)	C(1)–Rh(2)–C(10)	81.3(7)
Rh(1)–Rh(2)–C(13)	174.0(5)	C(1)–Rh(2)–C(11)	112.5(7)
Rh(1)–Rh(2)–C(14)	145.5(5)	C(1)–Rh(2)–C(13)	136.6(7)
Cl'–Rh(2)–N(2)	87.2(4)	C(1)–Rh(2)–C(14)	98.8(7)
Cl'–Rh(2)–C(1)	135.0(5)	C(10)–Rh(2)–C(11)	36.2(7)
Cl'–Rh(2)–C(10)	118.0(5)	C(10)–Rh(2)–C(13)	75.9(7)
Cl'–Rh(2)–C(11)	82.6(5)	C(10)–Rh(2)–C(14)	65.2(7)
Cl'–Rh(2)–C(13)	88.4(5)	C(11)–Rh(2)–C(13)	65.2(7)
Cl'–Rh(2)–C(14)	126.1(5)	C(11)–Rh(2)–C(14)	78.9(7)
N(2)–Rh(2)–C(1)	86.0(6)	C(13)–Rh(2)–C(14)	38.0(7)

(c) In the carbonyl groups

C(1)–O(1)	1.128(21)	C(2)–O(2)	1.141(23)

Rh(1)–C(1)–Rh(2)	83.9(7)	Rh(1)–C(2)–O(2)	177(2)
Rh(1)–C(1)–O(1)	139(2)	Rh(2)–C(1)–O(1)	137(2)

(d) In the ligand L

N(1)–C(3)	1.37(3)	C(4)–C(5)	1.60(3)
N(1)–C(9)	1.36(2)	C(5)–C(6)	1.26(3)
N(2)–C(8)	1.36(3)	C(5)–C(9)	1.45(3)
N(2)–C(9)	1.35(2)	C(6)–C(7)	1.25(4)
C(3)–C(4)	1.42(3)	C(7)–C(8)	1.36(3)

Rh(1)–N(1)–C(3)	129(1)	C(4)–C(5)–C(9)	102(2)
Rh(1)–N(1)–C(9)	121(1)	C(6)–C(5)–C(9)	120(2)
C(3)–N(1)–C(9)	110(2)	C(5)–C(6)–C(7)	118(3)
Rh(2)–N(2)–C(8)	126(2)	C(6)–C(7)–C(8)	127(3)
Rh(2)–N(2)–C(9)	122(1)	N(2)–C(8)–C(7)	120(2)
C(8)–N(2)–C(9)	112(2)	N(1)–C(9)–N(2)	125(2)
N(1)–C(3)–C(4)	112(2)	N(1)–C(9)–C(5)	112(2)
C(3)–C(4)–C(5)	104(2)	N(2)–C(9)–C(5)	123(2)
C(4)–C(5)–C(6)	138(3)		

(e) In the ligand nbd

C(10)–C(11)	1.37(3)	C(12)–C(16)	1.55(3)
C(10)–C(15)	1.51(3)	C(13)–C(14)	1.42(3)
C(11)–C(12)	1.57(3)	C(14)–C(15)	1.57(3)
C(12)–C(13)	1.54(3)	C(15)–C(16)	1.57(3)

C(11)–C(10)–C(15)	110(2)	C(13)–C(14)–C(15)	104(2)
C(10)–C(11)–C(12)	104(2)	C(10)–C(15)–C(14)	100(2)
C(11)–C(12)–C(13)	99(2)	C(10)–C(15)–C(16)	100(2)
C(11)–C(12)–C(16)	102(2)	C(14)–C(15)–C(16)	101(2)
C(13)–C(12)–C(16)	100(2)	C(12)–C(16)–C(15)	94(2)
C(12)–C(13)–C(14)	109(2)		

* Primed atoms are related to the corresponding unprimed ones by an inversion centre (symmetry equivalent position: $-x$, $-y$, $-z$).

to form a unique strictly planar Rh_4Cl_2 ring [Rh(1), Rh(2), Cl', Rh(1)', Rh(2)', and Cl deviate from the mean plane passing through them by 0.004(2), $-0.002(2)$, 0.002(5), $-0.004(2)$, 0.002(2), and $-0.002(5)$ Å]. In each binuclear unit a bidentate anion L and a carbonyl group act as bridges between two directly bonded Rh atoms.

It is noteworthy that the two metal atoms present different co-ordination geometries. The Rh(1) atom displays an unusual distorted trigonal-bipyramidal co-ordination with the carbon atom of the terminal carbonyl group and the pyrrolic nitrogen atom N(1) of the ligand L in the apical positions and a chlorine atom, the carbon atom of the bridging carbonyl group, and the Rh(2) atom in the equatorial position. The co-ordination around the second rhodium atom, Rh(2), can be described as distorted octahedral, involving the midpoints of the olefinic bonds of the nbd ligand, the carbon atom of the bridging carbonyl group, the N(2) atom of ligand L, the Cl' and Rh(1) atoms.

The Rh(1)–Rh(2) distance [2.686(2) Å] is in the range of those expected for complexes with a Rh–Rh single bond, bridged by a carbonyl group and by a bidentate ligand (e.g. diphosphines,[15] 2-(diphenylphosphino)pyridine,[3] or cyclohexa-1,3-diene[16]). This bond could be interpreted as a donor bond from electron-rich Rh(2) to the electron-poor Rh(1), as suggested recently for the binuclear phosphidorhodium complexes.[17]

Also noteworthy is the relatively short Rh(1)–Rh(1') separation [3.156(2) Å]; it is shorter than the one found in $[Rh_2(\mu\text{-L})_2(nbd)_2]$ and could be indicative of a weak metal–metal interaction, as already postulated for related dimeric systems with similar intermetallic distances.[10]

The ligand L is planar [N(1), C(3), C(4), C(5), C(6), C(7), C(8), C(9), and N(2) deviate from the mean plane through them by $-0.01(1)$, $-0.02(2)$, 0.01(2), 0.01(2), 0.01(2), $-0.01(2)$ $-0.02(2)$, 0.02(2), and 0.02(1) Å respectively] and is nearly perpendicular to the Rh_4Cl_2 ring [dihedral angle 88.1(3)°]. It is bonded in the same way as in complex (13) with comparable Rh–N bond distances [2.088(13) and 2.067(14) Å in (21)]. The Rh(1), N(1), C(9), N(2), Rh(2) system is planar, these atoms deviating from the mean plane by 0.01(1), $-0.01(1)$, 0.01(1), 0.01(1), and $-0.01(1)$ Å. The carbonyl ligand asymmetrically bridges the two Rh atoms [Rh(1)–C(1) 1.97(2) and Rh(2)–C(1) 2.05(2) Å]. These distances are comparable with those reported for other rhodium(I) systems with bridging carbonyl ligands.[18] The Rh(1)–C(1)–Rh(2) angle [83.9(7)°] is in the range reported (80—93°) for complexes in which a carbonyl ligand bridges a metal–metal bond; values in the range 106—119° have been found in complexes with a carbonyl group bridging two non-bonded metals.[19]

The bonding of the nbd to the metal is quite regular, the Rh–C bonds ranging from 2.17(2) to 2.23(2) Å and the olefinic bond distances [C(10)–C(11) and C(13)–C(14)] being 1.37(3) and 1.42(3) Å.

Experimental

The complexes $[Rh_2Cl_2(\text{diolefin})_2]$ (diolefin = cod,[20] nbd,[21] tfbb,[22] or Me_3tfbb[22]), $[Ir_2Cl_2(cod)_2]$,[23] $[Rh_2Cl_2(CO)_4]$,[24] $[Rh(acac)(CO)_2]$,[25] and $[Rh(acac)(\text{diolefin})]$[26] were prepared according to literature methods. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. I.r. spectra (range 4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 597 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions in NaCl windows. Molecular weights were determined with a Hitachi–Perkin-Elmer 115 osmometer using chloroform solutions. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} acetone solutions using a Philips 9501/01 conductimeter.

The reactions were generally carried out at room temperature

under an atmosphere of oxygen-free nitrogen. Prior to use, solvents were purified by standard methods. Analytical and characteristic i.r. data of the compounds are reported in Table 1.

Preparations.—[MCl(diolefin)(HL)] (1)—(5). Solid ligand HL (24 mg, 0.2 mmol) was mixed with a solution of the complex [Rh$_2$Cl$_2$(diolefin)$_2$] (diolefin = cod, nbd, tfbb, or Me$_3$tfbb) or [Ir$_2$Cl$_2$(cod)$_2$] (0.1 mmol) in dichloromethane (5 cm^3). Concentration of these solutions to *ca.* 1 cm^3 and slow addition of hexane (10 cm^3) rendered the complexes (1)—(5) as microcrystalline solids, which were filtered off, washed with hexane, and vacuum-dried. Complexes (1) and (3) are scarcely soluble in methanol. They precipitate from the reaction mixture if their preparations are carried out in this solvent.

[MCl(CO)$_2$(HL)] [M = Rh (6) *or* Ir (7)]. Dry carbon monoxide was bubbled through a dichloromethane solution (3 cm^3) of complex (1) (72 mg, 0.2 mmol) or (5) (90 mg, 0.2 mmol) for 15 min. Hexane (10 cm^3) was then added and the bubbling was continued for 2 h to complete the crystallization of complex (6) and (7). Crystals were separated by filtration, washed with hexane, and vacuum-dried. Complex (6) can also be prepared by mixing solutions of [Rh$_2$Cl$_2$(CO)$_4$] (39 mg, 0.1 mmol) and HL (24 mg, 0.2 mmol) in dichloromethane (5 cm^3). Working up was as for complexes (1)—(5).

[Rh(diolefin)(HL)$_2$][ClO$_4$] (8)—(10). Solid HL (24 mg, 0.2 mmol) was mixed with a solution of the complex [Rh(diolefin)$_2$][ClO$_4$] (diolefin = cod, nbd, or tfbb) in dichloromethane (5 cm^3). Working up was as for complexes (1)—(5) using diethyl ether instead of hexane. Molar conductivities: complex (8), 133; (9) 127; and (10) 108 Ω^{-1} cm^2 mol^{-1}.

[Rh(CO)$_2$(HL)$_2$][ClO$_4$] (11). Dry carbon monoxide was bubbled through a yellow dichloromethane solution (10 cm^3) of complex (8) (55 mg, 0.1 mmol) for 2 h giving an orange solution. Diethyl ether (10 cm^3) was then added and the bubbling continued for *ca.* 2 h. Evaporated solvent was replaced with diethyl ether to yield complex (11) as white crystals. Molar conductivity: 131 Ω^{-1} cm^2 mol^{-1}.

[M$_2$(μ-L)$_2$(diolefin)$_2$] (12)—(15). The solid compound [Rh$_2$Cl$_2$(diolefin)$_2$] (diolefin = cod, nbd, or tfbb) (0.1 mmol) or [Ir$_2$Cl$_2$(cod)$_2$] (67 mg, 0.1 mmol) was added to a mixture of HL (24 mg, 0.2 mmol) and potassium hydroxide (0.2 mmol) in methanol (15 cm^3) to give orange or red suspensions of complexes (12)—(15). Stirring was continued for 30 min and then water (1 cm^3) was added to complete the precipitations. The solids were filtered off, washed with methanol–water (5:1), and vacuum-dried.

[Rh$_2$(μ-L)$_2$(CO)$_4$] (16). A mixture of [Rh(acac)(CO)$_2$] (52 mg, 0.2 mmol) and HL (24 mg, 0.2 mmol) in methanol (10 cm^3) was stirred for 30 min. Water (1 cm^3) was added to complete the precipitation of the compound. The solid was filtered off, washed with methanol–water (5:1), and vacuum-dried.

[Rh$_2$(μ-L)$_2$(CO)$_2$(PPh$_3$)$_2$] (17). A mixture of [Rh(acac)(CO)$_2$] (52 mg, 0.2 mmol) and HL (24 mg, 0.2 mmol) in dichloromethane (10 cm^3) was stirred for 30 min to give a red solution of complex (16). Solid PPh$_3$ (52 mg, 0.2 mmol) was added and the reaction was monitored by i.r. spectroscopy. After 2 h the spectrum showed a unique broad v(CO) band at 1 970 cm^{-1}. The solution was concentrated to *ca.* 2 cm^3 and chromatographed on an alumina column (20 × 1 cm). Elution with dichloromethane–hexane (2:1) afforded an orange band. Evaporation of the solvent and addition of hexane gave complex (17) as crystals which were separated by filtration.

[(diolefin)Rh(μ-L)$_2$Rh(CO)$_2$] (18)—(20). A mixture of [Rh$_2$(μ-L)$_2$(diolefin)$_2$] (0.1 mmol) and complex (16) (55 mg, 0.1 mmol) was refluxed in deoxygenated methanol (15 cm^3) for *ca.* 5 h. The volatiles were pumped off and the residue was extracted with dichloromethane (10 cm^3) and filtered. The extract was evaporated to *ca.* 1 cm^3 and either addition of cold hexane

[complex (18)] or successive addition of methanol (10 cm^3) and water (2 cm^3) [complexes (19)—(20)] led to the precipitation of microcrystalline solids which were separated by filtration. Complexes (18)—(20) can be recrystallized by slow evaporation of dichloromethane–hexane (1:2) solutions. Complex (18) δ(H) (200-MHz spectrum obtained on a Varian LX-200 spectrometer; in CDCl$_3$; SiMe$_4$ as reference 8.24 [2 H, d, ^3J(HH) 5.4], 7.58 [2 H, dd, ^3J(HH) 7.6, ^4J(HH) 1.3], 7.45 [2 H, d, ^3J(HH) 2.6], 6.66 [2 H, dd, ^3J(HH) 7.6, ^3J(HH) 5.4], 6.29 [2 H, d, ^3J(HH) 2.7 Hz], 4.25 (4 H, br s, olefinic H), 4.04 (2 H, br s, CH), and 1.26 (2 H, br s, CH$_2$).

[Rh$_4$(μ-Cl)$_2$(μ-L)$_2$(μ-CO)$_2$(CO)$_2$(nbd)$_2$] (21). In all methods described the resultant suspension was filtered and the solid washed with methanol and vacuum-dried.

Method (*a*). A mixture of compound (2) (70 mg, 0.2 mmol) and [Rh(acac)(CO)$_2$] (52 mg, 0.2 mmol) in methanol (5 cm^3) was stirred for 30 min to give an orange suspension. Yield: 86 mg, 85%.

Method (*b*). A mixture of compound (6) (31 mg, 0.1 mmol) and [Rh(acac)(nbd)] (29 mg, 0.1 mmol) in methanol (5 cm^3) was stirred for 30 min to afford an orange suspension. Yield: 80 mg, 80%.

Method (*c*). A mixture of compound (13) (62 mg, 0.1 mmol) and [Rh$_2$Cl$_2$(CO)$_4$] (39 mg, 0.1 mmol) in methanol–dichloromethane (5:1) (10 cm^3) was stirred for 30 min to give an orange suspension. Yield: 71 mg, 70%.

Method (*d*). A mixture of compound (16) (55 mg, 0.1 mmol) and [Rh$_2$Cl$_2$(nbd)$_2$] (46 mg, 0.1 mmol) in methanol (10 cm^3) was stirred for 1 h to give an orange suspension. Yield: 71 mg, 70%.

Reaction of Complex (21) *with Hydrochloric Acid.*—To a suspension of complex (21) (80 mg, 0.16 mmol) in dichloromethane–acetone (5:1) (6 cm^3) was added hydrochloric acid (13.6 μl, 11.8 mol dm^{-3} in water, 0.16 mmol) to give an orange solution. The solvent was pumped off and the oily residue disolved in dichloromethane (1 cm^3) and chromatographed on an alumina column (1 × 10 cm). Elution with dichloromethane–hexane (1:1) give a red band of complex (18).

Crystallography.—Single crystals suitable for *X*-ray diffraction studies were grown by slow diffusion of diethyl ether into dichloromethane solutions of complex (13) or (21).

Crystal data. Complex (13), C$_{28}$H$_{26}$N$_4$Rh$_2$, *M* = 624.35, monoclinic, *a* = 16.272(4), *b* = 7.932(2), *c* = 19.198(5) Å, β = 112.07(2)°, *U* = 2 296(1) Å^3 [by least-squares refinement of the θ values (26 ≤ θ ≤ 35°) of 30 accurately measured reflections, λ = 1.541 78 Å], space group *C*2/*c*, *Z* = 4, *D*$_c$ = 1.806 g cm^{-3}, *F*(000) = 1 248. A prismatic red-orange crystal with approximate dimensions 0.06 × 0.16 × 0.49 mm was used for data collection, μ(Cu-*K*$_\alpha$) = 120.85 cm^{-1}.

Complex (21), C$_{32}$H$_{26}$Cl$_2$N$_4$O$_4$Rh$_4$, *M* = 1 013.11, monoclinic, *a* = 11.091(3), *b* = 16.615(6), *c* = 8.531(4) Å, β = 91.63(3)°, *U* = 1 571(1) Å^3 [least-squares treatment of θ values (10 ≤ θ ≤ 15°) of 26 accurately measured reflections, λ = 0.710 69 Å], space group *P*2$_1$/*n*, *D*$_c$ = 2.141 g cm^{-3}, *Z* = 2, *F*(000) = 984. An orange-brown elongated prismatic crystal with approximate dimensions 0.06 × 0.12 × 0.35 mm was used for data collection, μ(Mo-*K*$_\alpha$) = 22.50 cm^{-1}.

Data collection and processing. Complex (13): Siemens AED diffractometer, θ—2θ mode, nickel-filtered Cu-*K*$_\alpha$ radiation; one standard reflection every 50 reflections, no significant change observed. 2 150 Independent reflections measured (3 ≤ θ ≤ 70°, ±*h*,*k*,*l*) 1 805 having *I* > 2σ(*I*) considered observed. Usual Lorentz and polarization reduction, absolute scale first by Wilson's method and then by least-squares refinement. Absorption ignored.

Complex (21): analogous data-collection procedure. Ni-

Table 4. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of the complex [Rh$_2$(μ-L)$_2$(nbd)$_2$]

Atom	X/a	Y/b	Z/c
Rh(1)	470(1)	2 654(1)	3 399(1)
N(1)	1 225(4)	817(8)	3 109(4)
N(2)	550(4)	905(9)	1 775(4)
C(1)	1 568(6)	3 953(12)	4 165(5)
C(2)	1 277(6)	4 810(12)	3 485(6)
C(3)	612(7)	6 154(14)	3 519(5)
C(4)	−172(6)	4 978(12)	3 488(6)
C(5)	121(6)	4 104(12)	4 169(6)
C(6)	1 077(7)	4 729(13)	4 640(6)
C(7)	1 009(8)	6 602(12)	4 372(5)
C(8)	1 905(6)	−54(12)	3 652(6)
C(13)	641(7)	116(13)	1 153(6)
C(14)	1 147(5)	292(9)	2 437(5)
C(9)	2 326(14)	−1 175(28)	3 298(13)
C(10)	1 802(10)	−1 002(19)	2 522(10)
C(11)	1 835(13)	−1 709(25)	1 872(11)
C(12)	1 244(13)	−991(25)	1 163(12)
C(15)	2 392(19)	−1 222(36)	3 568(18)
C(16)	2 330(15)	−1 765(31)	2 809(13)
C(17)	1 657(13)	−927(24)	2 194(14)
C(18)	1 337(17)	−1 199(33)	1 432(17)

Table 5. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms of the complex [Rh$_4$(μ-Cl)$_2$-(μ-L)$_2$(μ-CO)$_2$(CO)$_2$(nbd)$_2$]

Atom	X/a	Y/b	Z/c
Rh(1)	1 025(1)	477(1)	924(1)
Rh(2)	2 377(1)	149(1)	−1 559(1)
Cl(1)	−513(4)	606(3)	2 832(5)
O(1)	3 538(11)	978(8)	1 187(14)
O(2)	292(12)	2 053(8)	−468(16)
N(1)	1 632(12)	−626(8)	1 815(15)
N(2)	2 810(12)	−919(8)	−434(15)
C(1)	2 740(16)	690(10)	560(19)
C(2)	542(15)	1 441(11)	55(20)
C(3)	1 372(16)	−983(11)	3 215(21)
C(4)	1 942(20)	−1 746(13)	3 382(26)
C(5)	2 687(19)	−1 838(12)	1 810(23)
C(6)	3 388(22)	−2 338(15)	1 198(30)
C(7)	3 806(20)	−2 167(13)	−105(26)
C(8)	3 578(16)	−1 492(11)	−963(21)
C(9)	2 373(14)	−1 105(10)	981(19)
C(10)	2 783(16)	1 383(11)	−2 412(21)
C(11)	1 967(16)	1 024(11)	−3 432(21)
C(12)	2 768(16)	632(11)	−4 713(20)
C(13)	3 331(15)	−51(11)	−3 726(20)
C(14)	4 132(16)	287(11)	−2 582(21)
C(15)	4 057(16)	1 217(11)	−2 907(21)
C(16)	3 851(18)	1 219(12)	−4 739(23)

obium-filtered Mo-K_α radiation; 2 184 independent reflections measured ($3 \leqslant \theta \leqslant 23°$, $\pm h,k,l$), 1 201 considered observed [$I > 2\sigma(I)$].

Structure analysis and refinement. Complex (13): Patterson and Fourier methods. The ligand HL was disordered, distributed in two positions with occupancy factors of 0.6 [C(9)—C(12)] and 0.4 [C(15)—C(18)] respectively, as both nitrogen atoms from the five- and six-membered rings are involved in co-ordination to the same metal. Due to the almost complete overlapping, it was not possible to separate some atoms [C(18), C(13), and C(14)] in the disordered ligand. Full-matrix least-squares refinement, anisotropic thermal parameters for all the non-hydrogen atoms, except the atoms involved in disorder [C(9)—C(12) and C(15)—C(18)]. The hydrogens of the diolefin

and the ligand with higher occupancy factor were clearly found from a ΔF map. These hydrogens were included in the final calculation, but not refined. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; weighting scheme, $w = 1/|\sigma^2(F_o) + 0.005F_o^2|$. Final R and R' values 0.072 and 0.074. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 4.

Complex (21): the crystal structure was solved by Patterson and Fourier methods. Full-matrix least-squares refinement, anisotropic thermal parameters for the metals and seven other atoms (2 Rh, Cl, 2 O, 2 N, and 2 C). Hydrogen atoms were found from a Fourier difference map and refined. Unit weights in all stages of the refinement. Final R and R' values 0.041 and 0.047. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 5.

The atomic scattering factors (corrected for anomalous dispersion of Rh and Cl) were taken from ref. 27. All calculations were performed with the SHELX system of computer programs[28] on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna with financial support from the University of Parma.

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