

Tri-, Bi- and Mononuclear Rhodium Complexes with the Anionic Polydentate Ligands 1,8-Naphthyridine-2-one and 5,7-Dimethyl-1,8-naphthyridine-2-one

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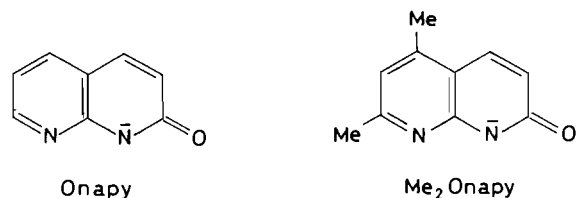
Abstract

The complexes of the general formula $[\{\text{Rh}(\text{R}_2\text{-Onapy})(\text{diolefin})\}_x]$ (diolefin = cod, tfb, nbd; Onapy = 1,8-naphthyridine-2-one) are prepared by reaction of $[\{\text{RhCl}(\text{diolefin})\}_2]$ with HR_2Onapy and potassium hydroxide; complexes with substituted R_2Onapy are mononuclear and those with Onapy are either mono- or binuclear. Both react with carbon monoxide to give $[\{\text{Rh}(\mu\text{-R}_2\text{Onapy})(\text{CO})_2\}_2]$ ($\text{R} = \text{H}, \text{Me}$). Reactions of these tetracarbonyl complexes with the species $[\text{Rh}(\text{CO})_2(\text{Me}_2\text{CO})_x]^+$ or with $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]\text{ClO}_4$ give the trinuclear complexes $[\text{Rh}_3(\mu_3\text{-R}_2\text{Onapy})_2(\text{CO})_6]\text{ClO}_4$ and $[\text{Rh}_3(\mu_3\text{-R}_2\text{Onapy})_2(\text{CO})_4(\text{PPh}_3)_2]\text{ClO}_4$, respectively. The former reacts with diolefins to give the complexes $[\text{Rh}_3(\mu_3\text{-R}_2\text{Onapy})_2(\text{CO})_2(\text{diolefin})_2]\text{ClO}_4$ (diolefin = cod, tfb, nbd). The bi- and trinuclear complexes are deeply-coloured solids which display a strong band in the visible region indicative of intramolecular metal–metal interaction.

Introduction

The preparation and properties of bi- and trinuclear complexes containing rhodium centres in close proximity are receiving a great deal of attention [1–4]. We have recently reported some com-

plexes with binucleating ligands containing N—C—N bridging units such as 1,8-naphthyridine [5] or the anionic forms of 7-azaindole [6] and *N,N'*-diphenylbenzamidine [7]. We report, in full, the coordinative behaviour of the polydentate ligands 1,8-naphthyridine-2-one (Onapy) and 5,7-dimethyl-1,8-naphthyridine-2-one (Me₂Onapy).



dine-2-one (Me₂Onapy). These anionic ligands should present the binucleating ability of the parent 1,8-naphthyridine along with an additional oxygen atom able to coordinate, the three donor atoms being coplanar. Thus, they could be, in principle, useful for the design of rigid trimetallic systems in which the metals are within cooperative distances. Part of the work concerning the 1,8-naphthyridine-2-one ligand has been the subject of a preliminary communication [8].

Experimental

The compounds $[\{\text{RhCl}(\text{diolefin})\}_2]$ (diolefin = cod [9], nbd [10], tfb [11]), $[\{\text{RhCl}(\text{CO})_2\}_2]$ [12], $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]\text{ClO}_4$ [13], $[\{\text{Rh}(\text{OMe})(\text{cod})\}_2]$ [14] and 1,8-naphthyridine-2-(1H)-one [15] were prepared according to literature methods. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 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 l^{-1} acetone solutions using a Philips 9501/01 conductimeter. Visible–ultraviolet spectra were run with a Cary 17 spectrophotometer on chloroform solutions of the complexes (in the 700–330 nm region).

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 IR data of the compounds are reported in Tables I and II.

Syntheses of Complexes

$[\text{Rh}(\text{R}_2\text{Onapy})(\text{diolefin})]_x$ ($x = 1$ (I), (IV–VI); $x = 2$ (II, III))

The solid compound $[\{\text{RhCl}(\text{diolefin})_2\}]$ (diolefin = cod, nbd, tfb) (0.1 mmol) was reacted with a

TABLE I. Colour, Analytical and Physical Data for the New Mono- and Binuclear Complexes

Compound	Colour	Yield (%)	Analyses (found(calculated) (%))			Molecular weight ^a	Visible absorption ^b (nm)
			C	H	N		
I [Rh(Onapy)(cod)]	yellow	80	54.10 (53.95)	4.80 (4.80)	7.60 (7.85)	389 (357)	
II [{Rh(μ -Onapy)(tfb)} ₂]	orange	70	49.65 (50.65)	2.40 (2.35)	5.60 (5.90)	846 (948)	525 (2.5 × 10 ³)
III [{Rh(μ -Onapy)(nbd)} ₂]·CH ₂ Cl ₂	dark-red	70	48.70 (48.65)	3.75 (3.70)	7.55 (7.30)	695 (765)	545 (3.0 × 10 ³)
IV [Rh(Me ₂ Onapy)(cod)]	yellow	70	56.20 (56.25)	5.50 (5.50)	7.40 (7.30)	406 (384)	
V [Rh(Me ₂ Onapy)(tfb)]	orange	80	53.05 (52.60)	3.40 (3.00)	5.30 (5.55)	524 (502)	
VI [Rh(Me ₂ Onapy)(nbd)]	red	60	54.60 (55.45)	4.65 (4.65)	7.35 (7.60)	386 (368)	
VII [{Rh(μ -Onapy)(CO) ₂] ₂]·0.5H ₂ O	dark-red	80	39.00 (38.90)	1.60 (1.80)	8.95 (9.05)	648 (627)	512 (4.5 × 10 ³)
VIII [{Rh(μ -Me ₂ Onapy)(CO) ₂] ₂]	dark-red	75	43.35 (43.40)	2.95 (2.75)	8.10 (8.45)	693 (664)	516 (3.5 × 10 ³)

^aIn chloroform; calculated values given in parentheses. ^b λ_{\max} values given with molar extinction coefficient (ϵ) in parentheses.

mixture of 1,8-naphthyridine-2(1H)-one (29 mg, 0.2 mmol) or 5,7-dimethyl-1,8-naphthyridine-2(1H)-one (35 mg, 0.2 mmol) and potassium hydroxide in methanol (2 ml, 0.1 mol l⁻¹ solution, 0.2 mmol) for 5 min at room temperature. The solvent was pumped off, the residue extracted with dichloromethane (complexes I, II, III, V), dichloromethane/diethyl ether (1:2) (complex IV), or diethyl ether (complex VI) and then filtered. Concentration of the filtrate to ca. 1 ml and slow addition of cold hexane rendered the complexes (I–VI) as microcrystalline solids which were filtered off, washed with hexane and vacuum-dried. Complex II crystallizes either with water as dark-red crystals or with diethyl ether when the red solid is stirred in diethyl ether for 15 min.

Alternatively, complexes I and II can also be prepared by mixing solutions of [{Rh(OMe)(diolefin)}₂] (0.1 mmol) and 1,8-naphthyridine-2-(1H)-one (0.2 mmol) in dichloromethane. Working up was as described above.

[{Rh(μ -R₂Onapy)(CO)₂]₂] (VII, VIII)

Dry carbon monoxide was bubbled through a dichloromethane solution (5 ml) of complex I (71 mg, 0.2 mmol) or IV (77 mg, 0.2 mmol) for 15 min. Hexane (10 ml) was then added and the bubbling was continued for 2 h to complete the crystallization of complexes. Crystals were separated by filtration, washed with hexane and vacuum-dried.

[Rh₃(μ ₃-R₂Onapy)₂(CO)₂(cod)₂] (XII, XIII)

A diluted acetone solution of [Rh(CO)₂(Me₂CO)_x]ClO₄ (prepared by treating [RhCl-

(CO)₂]₂] (20 mg, 0.05 mmol) with AgClO₄ (21 mg, 0.1 mmol) in acetone (10 ml) for 15 min and filtering off the AgCl formed) was added slowly to a solution of complex I (71 mg, 0.2 mmol) or IV (77 mg, 0.2 mmol) in dichloromethane (3 ml). The violet solutions were evaporated to dryness under vacuum, the residue extracted with dichloromethane, dried with magnesium sulfate and then filtered. Concentration of the filtrate to ca. 1 ml and slow addition of diethyl ether rendered the complexes as microcrystalline solids which were filtered off, washed with diethyl ether and vacuum-dried.

[Rh₃(μ ₃-Me₂Onapy)₂(CO)₆]ClO₄ (XI)

Dry carbon monoxide was bubbled through a violet dichloromethane/hexane (3:2) (10 ml) solution of complex XIII (77 mg, 0.2 mmol) for 2 h. The colour of the solution turned deep-blue, and dark-blue crystals of the title complex precipitated. The solvent was syringed out and the solid was washed with diethyl ether and vacuum-dried.

[Rh₃(μ ₃-R₂Onapy)₂(CO)₂(diolefin)₂]ClO₄ (XII–XVII)

An acetone solution of [Rh(CO)₂(Me₂CO)_x]ClO₄ prepared as described above was added to solutions of complex VII (62 mg, 0.1 mmol) or VIII (66 mg, 0.1 mmol) in dichloromethane to give deep-blue solutions of the hexacarbonyl species [Rh₃(μ ₃-R₂-Onapy)₂(CO)₆]⁺. The appropriate diolefin [cod (0.3 ml, 2.5 mmol), nbd (0.3 ml, 3 mmol), tfb (33 mg, 0.15 mmol)] was added. The solvent was pumped off and replaced by dichloromethane.

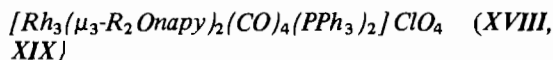
TABLE II. Colour, Analytical and Physical Data for the New Trinuclear Complexes

Compound	Colour	Yield	Analyses (found/calculated) (%)			λ_{m} ($\text{S cm}^{-2} \text{ mol}^{-1}$)	$\nu(\text{CO})$ (cm^{-1}) (in CH_2Cl_2)	Visible absorption ^a (nm)
			C	H	N			
XI	dark-blue	75	33.30 (33.85)	1.95 (1.95)	6.10 (6.10)	2110s, 2080s 2045s, 2020m	602 ^b	
XII	violet	70	41.50 (42.05)	3.50 (3.55)	6.10 (5.75)	2080s, 2020s	555 (12.5×10^3)	
XIII	violet	70	43.85 (44.45)	4.05 (4.10)	5.65 (5.45)	2075s, 2020s	576 (13.5×10^3)	
XIV	dark-blue	60	40.25 (40.95)	2.60 (2.80)	5.85 (5.95)	2080s, 2025s	604 (13×10^3)	
XV	dark-blue	60	41.25 (41.80)	1.95 (1.85)	4.80 (4.65)	2080s, 2025s	602 (13×10^3)	
XVI	dark-blue	65	44.00 (43.45)	3.60 (3.45)	5.65 (5.65)	2080s, 2025s	604 (13.5×10^3)	
XVII	dark-blue	65	43.65 (43.75)	2.55 (2.40)	4.55 (4.45)	2080s, 2025s	594 (14.5×10^3)	
XVIII	dark-blue	80	50.25 (50.20)	3.40 (2.95)	4.15 (4.10)	2075s, 2020s 1975vs	599 ^b	
XIX	dark-blue	70	49.50 (49.55)	3.45 (3.55)	3.80 (3.80)	2080s, 2020s 1970vs	623 ^b	

^a λ_{max} values given with molar extinction coefficients (ϵ) in parentheses. ^bDecomposes slowly.

The reactions were monitored by IR spectroscopy. After 2 h, the solutions were dried with magnesium sulfate and then filtered. Concentration of the filtrate to ca. 1 ml and addition of diethyl ether rendered the complexes as microcrystalline solids which were filtered off, washed with diethyl ether and vacuum-dried.

Complexes XVIII and XIX can also be prepared by this method by addition of triphenylphosphine in 2:1 molar ratio to the deep-blue solution of the hexacarbonyl complexes.



The solid compound $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{Me}_2\text{CO})] \cdot \text{ClO}_4$ (81 mg, 0.1 mmol) was added to a solution of the complex VII (62 mg, 0.1 mmol) or VIII (66 mg, 0.1 mmol) in dichloromethane and stirred for 15 min (complex XVIII) or 2 h (complex XIX). The resulting dark-blue solutions were concentrated to ca. 1 ml and slow addition of diethyl ether rendered the complexes as microcrystalline solids which were separated by filtration, washed with diethyl ether and vacuum-dried.

Results and Discussion

Mono- and Binuclear Complexes

Addition of 1,8-naphthyridine-2-(1H)-one (HOnapy) to dichloromethane solutions of the compounds $[\{\text{Rh}(\mu\text{-OMe})(\text{diolefin})\}_2]$ [14] gives rise immediately to the complexes $[\text{Rh}(\mu\text{-Onapy})(\text{diolefin})]_x$ [diolefin = 1,5-cyclooctadiene (cod), $x = 1$ (I) or tetrafluorobenzobarrelene (tfb), $x = 2$ (II)]. These complexes as well as the related 2,5-norbornadiene (nbd) derivative $[\text{Rh}(\mu\text{-Onapy})(\text{nbd})]_2$ (III) can be alternatively obtained by reaction of the appropriate $[\{\text{RhCl}(\text{diolefin})\}_2]$ complex with HOnapy and potassium hydroxide in methanol. For diolefin = cod, the formation of a suspension of $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ is observed in this second route, which is in accordance with the very weak acid strength of HOnapy. Removal of methanol and subsequent use of non-donor solvents renders the complexes I–III in high yield. The compounds show a marked tendency to crystallize with molecules of solvent and have been identified by elemental analysis, molecular weight measurements (Table I), and IR and NMR spectroscopy.

The mononuclear complexes $[\text{Rh}(\text{Me}_2\text{Onapy})(\text{diolefin})]$ [diolefin = cod (IV) tfb (V), nbd (VI)] are obtained by reaction of the appropriate $[\{\text{RhCl}(\text{diolefin})\}_2]$ complex with a methanolic solution of HMe_2Onapy and potassium hydroxide. Molecular weight determinations support their formulation as mononuclear complexes.

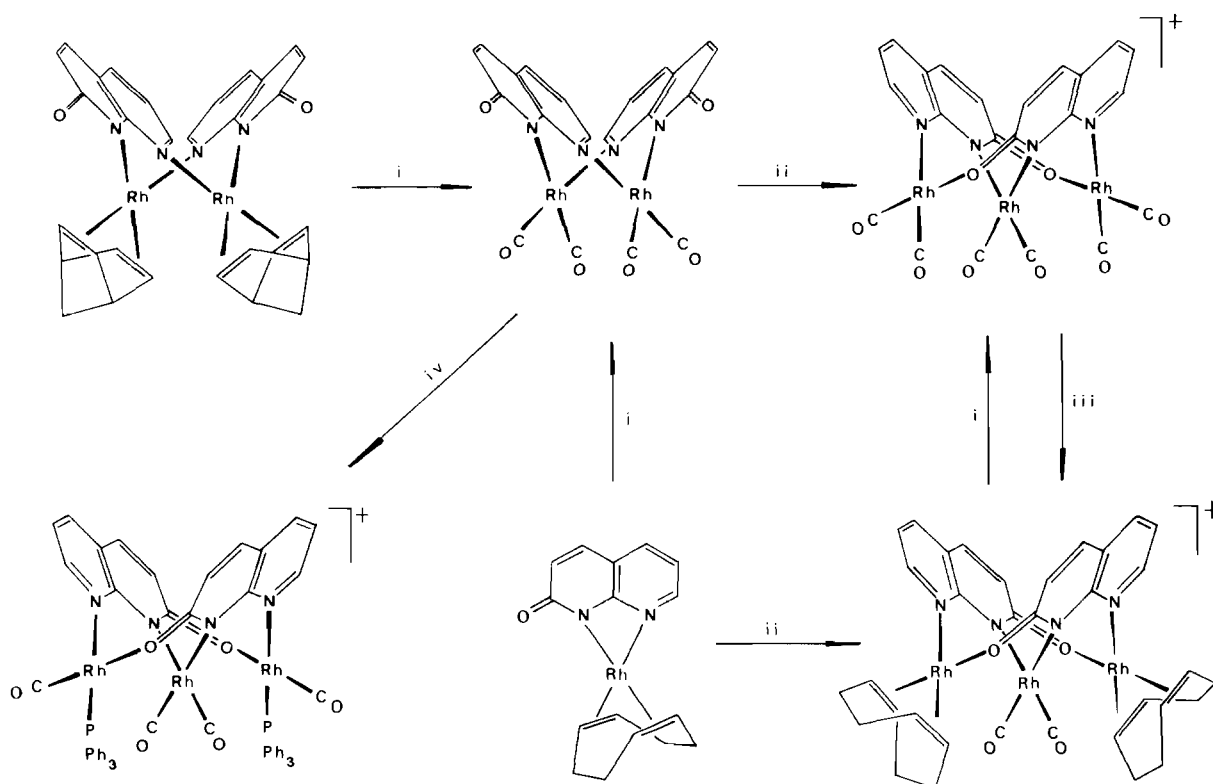
The 200 MHz ^1H NMR spectrum of the mononuclear complex **IV** at 20 °C in CDCl_3 shows sharp resonances for the Me_2Onapy group [at δ 7.47(d,1H), 6.46(d,1H), 6.43(s,1H), 2.36(s,3H) and 2.09(s,3H)], two multiplets (at δ 2.47 and 1.82) for the methylene protons and an unresolved band at δ 4.88 for the olefinic protons of cod. At -50 °C, in the slow-exchange region, the ^1H NMR spectrum displays the same resonances as above except two signals of relative intensity 2:2 at δ 5.22 and 4.51, which collapse at *ca.* 0 °C and emerge as the time-averaged band at δ 4.88. The low temperature spectrum is in accordance with a single species in solution having a square-planar structure in which Me_2Onapy acts as a chelating ligand probably through both nitrogen atoms; the magnetic nonequivalence of the two pairs of olefinic protons is imposed by the amide and pyridine character of the nitrogen atoms and the asymmetry of the ligand Me_2Onapy .

The 200 MHz ^1H NMR spectra of the complexes **I–III** in CDCl_3 at room temperature exhibit five resonances for the protons of the Onapy ligand and one unresolved band for the olefinic protons, indicative of a fluxional behaviour. The spectrum of the mononuclear complex **I** at -50 °C in CDCl_3 displays a large number of signals for the Onapy ligands and the olefinic protons owing to several species in solution. These species could be due to

a different type of coordination of the Onapy ligand ($\text{N} \leftarrow \text{C} \leftarrow \text{N}$ and $\text{N} \leftarrow \text{C} \leftarrow \text{O}$) in the mononuclear species at low temperature. In addition, an equilibrium between mono- and polynuclear complexes should be operating as observed for the related $[\text{Rh}(\text{triazenide})(\text{diolefin})]_x$ complexes [16].


The ^1H NMR spectrum of the binuclear complex **II** in CDCl_3 at -45 °C displays five sharp resonances due to the protons of the Onapy ligands [at δ 8.61(d, 2H, H^7), 7.68(d,2H, H^5), 7.20(d,2H, H^3), 7.02(t,2H, H^6), 6.25(d,2H, H^4)], four signals for the olefinic protons [at δ 4.5(overlapping m,4H) 3.60(m, three lines, 2H), 3.50(m, three lines, 2H)] and one sharp resonance without fine structure for the tertiary protons [at δ 6.23(4H)]. Since the resonances and $\nu(\text{C}=\text{O})$ of the Onapy ligands are slightly shifted from those of the free ligand, which is in the tautomeric keto form in solution, the Onapy ligands should be binucleating through the nitrogen atoms. The ^1H NMR spectrum of complex **II** is therefore consistent with a frozen structure, having a C_2 symmetry axis similar to that depicted in Scheme 1 for the nbd derivative; the main magnetic nonequivalence of the olefinic protons arises from their positions *trans* to either the amide or pyridinic nitrogen atoms.

It is noteworthy that the coordination mode (*i.e.*, binucleating or chelate) of the 1,8-naphthyltri-



Scheme 1. *i* = CO; *ii* = $[\text{Rh}(\text{CO})_2(\text{Me}_2\text{CO})_x]^+$; *iii* = cod; *iv* = $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]^+$.

dine-2-one ligand as well as other nitrogen-donor

ligands containing N  units such as 2-methyl-1,8-naphthyridine [5] or *N,N'*-diphenylbenzamidinate [7] in rhodium complexes depends on the ancillary diolefin in such a way that the combination of the lower π -acceptor ability and bigger steric hindrance of the 1,5-cyclooctadiene ligand, in comparison with the other diolefins studied, is in favour of the chelating mode (mononuclear species). In contrast, binuclear complexes (binucleating mode) are isolated with the less steric-demanding and stronger π -acceptor diolefins 2,5-norbornadiene and tetrafluorobenzobarrelene. This differential behaviour has been confirmed recently by the X-ray structure of the complexes $[\text{Rh}\{\mu\text{-PhC}(\text{NPh})_2\}(\text{diolefin})]_x$ (diolefin = cod, $x = 1$; tfb, $x = 2$) [7]. Moreover, the mononuclear nature of the complexes with the Me_2Onapy ligand (IV, V, VI), for all the diolefins, is probably related to the presence of the methyl group in position seven, which could produce steric hindrance with the coordinated diolefin in the hypothetical binuclear complexes $[\text{Rh}(\mu\text{-Me}_2\text{Onapy})(\text{diolefin})]_2$. In this context, it is of interest to recall [5] that only mononuclear diolefin rhodium complexes were isolated with the 2,7-dimethyl-1,8-naphthyridine ligand, whilst mono- and binuclear diolefin rhodium complexes are obtained with 2-methyl-1,8-naphthyridine and 1,8-naphthyridine.

Bubbling carbon monoxide through dichloromethane solutions of complexes I–III gives rise to the formation of the violet tetracarbonyl compound $[\{\text{Rh}(\mu\text{-Onapy})(\text{CO})_2\}_2] \cdot 0.5\text{H}_2\text{O}$ (VII), which decomposes slowly in the solid state and in solution. Its IR spectrum shows three $\nu(\text{CO})$ bands at 2085vs, 2055s and 2017vs cm^{-1} (in CH_2Cl_2) which is in accordance with the C_2 symmetry of the structure of this complex (see Scheme 1) assuming that the lowest-energy band contains two active $\nu(\text{CO})$ modes.

The electronic spectra of the binuclear complexes II, III and VII display an intense band in the 540–510 nm region which is not observed in those of the mononuclear complexes, suggesting that the rhodium atoms are in close proximity [17]. Thus, the X-ray structure of the complex VII confirms [8a] the approximately face to face disposition of the nearly square-planar environments of the rhodium atoms with a short metal–metal distance [2.880(2) Å]. The related deeply-coloured binuclear complex $[\{\text{Rh}(\mu\text{-Me}_2\text{Onapy})(\text{CO})_2\}_2]$ (VIII) [$\nu(\text{CO}) = 2085\text{vs}, 2055\text{s}, 2013\text{ vs cm}^{-1}$ (in CH_2Cl_2)] is also obtained by carbonylation of the mononuclear diolefin complexes IV–VI.

The influence of electronic and steric effects of the ligands on the nuclearity of the complexes with R_2Onapy is evident again if the tetracarbonyl complexes VII and VIII are compared with the diolefin complexes I–VI.

Trinuclear Complexes

The above mentioned mono- and binuclear complexes still have at least one uncoordinated ketonic oxygen atom and therefore are potential ligands. Thus, the reaction of the cationic solvated species $[\text{RhL}_2(\text{Me}_2\text{CO})_x]^+$ with dichloromethane solutions of complex VII in molar ratio 1:1 gives the presumably trinuclear deep-blue complexes $[\text{Rh}_3(\mu_3\text{-Onapy})_2(\text{CO})_4\text{L}_2]\text{ClO}_4$ [$\text{L} = \text{CO}$ (IX), $\text{L}_2 = \text{cod}$ (X)] which have not been isolated in pure state. Dichloromethane solutions of complex IX show $\nu(\text{CO})$ at 2115s, 2085s, 2050s and 2025m cm^{-1} and can be used for preparative purposes (*vide infra*). The related complex $[\text{Rh}_3(\mu_3\text{-Me}_2\text{Onapy})_2(\text{CO})_6]\text{ClO}_4$ (XI) is formed in solution by a similar reaction and can be isolated as a crystalline solid. Complex XI shows a pattern of $\nu(\text{CO})$ bands the same as that of solutions of complex IX (see Table II).

Attempts to purify complex X by recrystallization from 1,2-dichloroethane-diethyl ether gave violet crystals of $[\text{Rh}_3(\mu_3\text{-Onapy})_2(\text{CO})_2(\text{cod})_2]\text{-ClO}_4 \cdot 1.5\text{C}_2\text{H}_4\text{Cl}_2$ (XII) along with a black insoluble residue. Interestingly, complex XII and the related compound $[\text{Rh}_3(\mu_3\text{-Me}_2\text{Onapy})_2(\text{CO})_2(\text{cod})_2]\text{ClO}_4$ (XIII) are easily formed and isolated in good yield from the mononuclear complexes I or IV and $[\text{Rh}(\text{CO})_2(\text{Me}_2\text{CO})_x]\text{ClO}_4$ if the solvated dicarbonylrhodium species is added to a solution of the appropriate diolefin complex in a molar ratio of 1:2. Deep-blue solutions presumably of complex X are obtained if the order of addition is reversed.

The suggested structure (see Scheme 1) for the cation $[\text{Rh}_3(\mu_3\text{-Onapy})(\text{CO})_2(\text{cod})_2]^+$ has been confirmed by X-ray methods [8b]. The cation shows the three rhodium atoms in an approximately linear disposition in a face to face to face arrangement with Rh–Rh distances in the range 2.907(3)–2.912(2) Å, indicative of metal–metal interaction.

The trinuclear deeply-coloured complexes of formula $[\text{Rh}_3(\mu_3\text{-R}_2\text{Onapy})(\text{CO})_2(\text{diolefin})_2]\text{ClO}_4$ [$\text{R} = \text{H}$; diolefin = cod (XII), nbd (XIV), tfb (XV); $\text{R} = \text{Me}$, diolefin = cod (XIII), nbd (XVI), tfb (XVII)] are obtained by reaction of the appropriate diolefin with a solution of the hexacarbonyl complex $[\text{Rh}_3(\mu_3\text{-R}_2\text{Onapy})(\text{CO})_6]^+$ prepared *in situ* as described above. The complexes are 1:1 electrolytes in acetone solution and show two $\nu(\text{CO})$ bands (Table II) characteristic of an isolated *cis*-dicarbonylrhodium moiety. As expected, the hexacarbonyl complexes IX and XI are formed in solution by carbonylation of complexes XII and XIII, respectively, and XI is isolated as a pure solid by this method.

The formation of a tetranuclear rhodium complex can be envisaged if each ketonic oxygen in complex VII acts as a donor to a species having an easily replaceable ligand such as $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{Me}_2\text{CO})]\text{ClO}_4$ [13]. Nevertheless, the reaction of acetone solutions of these complexes immediately

gives the trinuclear complex $[\text{Rh}_3(\mu_3\text{-Onapy})_2(\text{CO})_4(\text{PPh}_3)_2]\text{ClO}_4$ (**XVIII**) which is isolated in good yield. Complex **XVIII** exhibits three $\nu(\text{CO})$ bands and its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays one signal doublet at δ 48.3 ($^1J(\text{RhP}) = 164$ Hz) for both phosphorus nuclei in accordance with the symmetrical structure depicted in Scheme 1. The PPh_3 groups are probably *trans* to the N atoms of the Onapy ligands according to the proposed *trans* effect of the nitrogen atom which is larger in comparison with the oxygen atom in comparable systems [18]. This reaction implies the migration of one coordinated PPh_3 group from one end of the complex cation to the other and should take place through dissociation. In fact, the reaction of the species $[\text{Rh}_3(\mu_3\text{-R}_2\text{Onapy})_2(\text{CO})_6]^+$ with triphenylphosphine in an acetone–dichloromethane mixture renders the complexes **XVIII** and **XIX**.

All the trinuclear complexes are deeply coloured in the solid state and in solution. They display a very intense absorption in the visible spectrum at lower energies than the binuclear complexes indicative of intramolecular metal–metal interactions between the three metal centres in close proximity as found for complex **XII**.

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