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Synthesis and crystal structure of $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$

Maddalena Pizzotti, Francesca Porta, Sergio Cenini

Dipartimento di Chimica Inorganica e Metallorganica and CNR Center, Via Venezian 21, 20133 Milano (Italy)

and Francesco Demartin

Istituto di Chimica Strutturistica Inorganica and CNR Center, Via Venezian 21, 20133 Milano (Italy)

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Abstract

Reaction of $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ with DPPM (diphenylphosphinomethane) has given the substituted imido complex $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$, the structure of which has been determined by X-ray diffraction. The compound crystallizes in the monoclinic space group $P2_1/n$ with a 14.027(7), b 14.887(7), c 18.499(9) Å, β 93.52(4)° and $Z = 4$; $R = 0.022$ and $R_w = 0.028$ for 5006 independent reflections with $I > 3\sigma(I)$. The interaction of the imido complex with CO has been investigated under various conditions. It proved to be very robust, giving small amounts of PhNCO (or $PhNHCO_2Me$ in the presence of methanol) and $Ru_3(\mu\text{-DPPM})(CO)_{10}$ only at 170 °C and 60 atm of carbon monoxide.

Introduction

Recently we reported that $Ru_3(CO)_{12}$ in the presence of DPPM (diphenylphosphinomethane) or other chelating ligands, and also the preformed cluster $Ru_3(\mu\text{-DPPM})(CO)_{10}$ are catalysts for the reductive carbonylation of nitrobenzene in toluene/methanol at 170 °C and 60 atm of carbon monoxide to give the corresponding carbamate, $PhNHCO_2Me$ [1].

We also reported that imido complexes of ruthenium, such as $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ and $Ru_3(\mu_3\text{-NPh})_2(CO)_9$, which are formed by reaction of nitrobenzene with $Ru_3(CO)_{12}$ [2], are key intermediates in the reductive carbonylation of aromatic nitro compounds catalysed by $Ru_3(CO)_{12}$ in the presence of $NEt_4^+\ Cl^-$ as co-catalyst [3]. We thus decided to study the synthesis and reactions of the imidoruthenium complex bearing the DPPM ligand, $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$. The structural features of the related imido-cluster complexes, $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ [4], $Ru_3(\mu_3\text{-}$

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$NPh)_2(CO)_9$ [5] and $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}DPPM)(CO)_7$ [6] have been reported previously. In the mono-imido complexes the triangle of ruthenium atoms remains intact, while in the bis-imido complexes the presence of another 4e donor imido ligand induces opening of one Ru–Ru bond. In $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}DPPM)(CO)_7$, the DPPM ligand spans the non-bonded Ru- - -Ru vector.

Results

(i) X-ray structure of $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$

The $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ structure consists of a triangular Ru_3 cluster μ_3-capped on opposite sides of the triangle by the NPh ligand and by one CO group (Fig. 1). The remaining CO groups are terminally bound and the bidentate DPPM ligand spans one edge of the metal triangle. The molecule can be regarded as derived from the parent $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ by replacement of two equatorial carbonyls by the DPPM ligand, resulting in a lowering of the idealized symmetry from C_{3v} to C_s. If the μ_3-NPh ligand is regarded as a four electron donor, the compound is a 48 valence electron molecule, and therefore all the Ru–Ru distances are bonding interactions; 50 valence electron complexes containing two μ_3-arylimido ligands capping a triangular cluster show an opening of one side of the triangle owing to the need to accomodate two extra electrons in antibonding cluster orbitals. The two stereochemically equivalent Ru(1)–Ru(3) and Ru(2)–Ru(3) distances are identical (2.743(1) Å) (Table 1), and are in keeping with the average Ru–Ru bond length in $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ [4]. The lengthening of the Ru(1)–Ru(2) distance to 2.787(1) Å is related to the bite requirements and steric repulsions of the DPPM ligand. Nevertheless the bond length is shorter than that of 2.854 Å found for

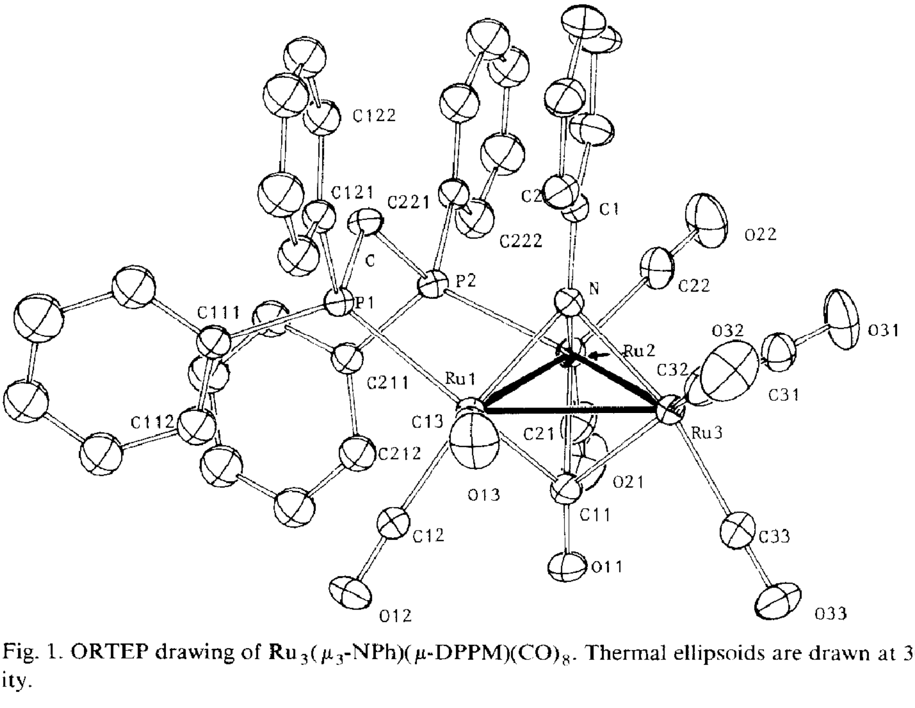

Fig. 1. ORTEP drawing of $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$. Thermal ellipsoids are drawn at 30% probability.

Table 1

Selected bond distances (Å) and angles (°) with their e.s.d.'s in parentheses

Ru(1)-Ru(2)	2.787(1)	Ru(1)-Ru(2)-Ru(3)	59.48(1)
Ru(1)-Ru(3)	2.743(1)	Ru(1)-Ru(3)-Ru(2)	61.07(1)
Ru(2)-Ru(3)	2.743(1)	Ru(2)-Ru(1)-Ru(3)	59.45(1)
Ru(1)-P(1)	2.305(1)	Ru(1)-N-Ru(2)	84.71(9)
Ru(2)-P(2)	2.383(1)	Ru(2)-N-Ru(3)	83.03(9)
		Ru(3)-N-Ru(1)	83.13(9)
Ru(1)-N	2.067(3)	Ru(1)-N-C(1)	133.6(2)
Ru(2)-N	2.070(3)	Ru(2)-N-C(1)	130.1(2)
Ru(3)-N	2.068(2)	Ru(3)-N-C(1)	124.8(2)
Ru-N(av)	2.068	P(1)-C-P(2)	111.2(2)
		Ru(1)-P(1)-C	112.8(1)
Ru(1)-C(11)	2.165(3)	Ru(2)-P(2)-C	109.9(1)
Ru(2)-C(11)	2.138(3)	Ru(1)-P(1)-C(111)	117.8(1)
Ru(3)-C(11)	2.200(3)	Ru(1)-P(1)-C(121)	113.1(1)
Ru-C(11)(av)	2.168	C-P(1)-C(111)	105.4(1)
C(11)-O(11)	1.181(4)	C-P(1)-C(121)	103.1(1)
		C(111)-P(1)-C(121)	103.2(1)
Ru(1)-C(12)	1.892(4)	Ru(2)-P(2)-C(211)	122.4(1)
Ru(1)-C(13)	1.919(4)	Ru(2)-P(2)-C(221)	114.2(1)
Ru(2)-C(21)	1.895(3)	C(211)-P(2)-C(221)	101.0(2)
Ru(2)-C(22)	1.889(4)	C-P(2)-C(211)	104.3(2)
Ru(3)-C(31)	1.937(4)	C-P(2)-C(221)	102.8(1)
Ru(3)-C(32)	1.896(4)		
Ru(3)-C(33)	1.915(4)	P(1)-C-P(2)-C(221)	156.6
Ru-C(av)	1.906	P(2)-C-P(1)-C(121)	177.1
C(12)-O(12)	1.140(4)		
C(13)-O(13)	1.134(4)		
C(21)-O(21)	1.138(4)		
C(22)-O(22)	1.146(4)		
C(31)-O(31)	1.129(5)		
C(32)-O(32)	1.130(4)		
C(33)-O(33)	1.130(4)		
C-O(av)	1.135		
N-C(1)	1.423(4)		
P(1)-C	1.833(3)		
P(2)-C	1.848(3)		

$Ru_3(CO)_{12}$ [7], where the elongation may be caused by steric repulsion between all the axial carbonyls. The two Ru–P distances are significantly different (2.305(1) vs. 2.383(1) Å); their average value, 2.344 Å, is only slightly larger than 2.322 Å in $Ru_3(\mu_3\text{-}NPh)_2(\mu\text{-}DPPM)(CO)_7$ [6]. Packing effects can account for this difference. The three Ru–N distances are equivalent within one esd and their mean value, 2.068 Å, can be compared with the value of 2.055 Å in $Ru_3(\mu_3\text{-}NPh)(CO)_{10}$ [4]. A slight asymmetry is found in the $Ru\text{–}CO_{(bridg.)}$ distances. All the other molecular parameters are normal.

(ii) Reactions of $Ru_3(\mu_3\text{-}NPh)(\mu\text{-}DPPM)(CO)_8$ with carbon monoxide

It has been recently reported that carbonylation of $Ru_3(\mu_3\text{-}NPh)_x(CO)_{11-x}$ ($x = 1, 2$) in acetonitrile at 140 °C with ca. 20 atm of CO for 3 h gives quantitative yields of $Ru_3(CO)_{12}$ and PhNCO [8]. We have found that the carbonylation of $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$ in dry acetonitrile at 140 °C and 20 atm of carbon monoxide for 3 h leaves the imido complex unchanged. Even at 60 atm of carbon monoxide, no reaction was observed.

Reaction was observed only at 170 °C under 60 atm of carbon monoxide for 5 h in dry benzene, and gave small amounts of phenylisocyanate and $Ru_3(\mu\text{-DPPM})(CO)_{10}$ [eq. (1)]:

$$Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8 + 3CO \rightarrow PhNCO + Ru_3(\mu\text{-DPPM})(CO)_{10} \qquad (1)$$

When the reaction was carried out in the presence of methanol, the corresponding carbamate, $PhNHCO_2Me$, rather than the isocyanate was detected as the product by gas-chromatographic analysis. However in both cases, the reactions leave most of the starting material unchanged. In a reaction carried out in the absence of methanol, a small amount of aniline was detected, possibly owing to the presence of traces of moisture. It is evident that the presence of the DPPM ligand in the complex inhibits the attack on the imido group by carbon monoxide. This could be due to a strengthening of the metal–carbon bond to the remaining carbonyls when two of them are replaced by the more basic DPPM ligand. On the other hand the presence of this ligand in the cluster does not induce any significant change in the bonding of the triply-bridging imido ligand to the three ruthenium atoms.

On the basis of these results we conclude that a species such as $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$ is not involved in the catalytic carbonylation of nitrobenzene catalysed by $Ru_3(\mu\text{-DPPM})(CO)_{10}$ [1].

Experimental

The reactions at atmospheric pressure were carried out under dinitrogen with magnetic stirring. The complex $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ was prepared as described in the literature [2]. All solvents were dried, purified, and stored under nitrogen. Infrared spectra were recorded on a Beckman 4210 and on a FT Nicolet MX-1 spectrophotometers. ^1H and ^{31}P NMR spectra were recorded on a Bruker VP 80 spectrometer. Elemental analyses were carried out in the analytical laboratories of Milan University.

Gas-chromatographic analyses were carried out with a PS 255, 15 m capillary column using a Carlo Erba gas-chromatograph connected with a Perkin–Elmer data system, with hexamethylbenzene as internal standard.

Synthesis of $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$

To $Ru_3(\mu_3\text{-NPh})(CO)_{10}$ (133 mg, 0.197 mmol), DPPM (78 mg, 0.203 mmol) and THF (65 ml) were added. After 30 min, a small amount of $PPN^+ AcO^-$ was added to the yellow solution, which gradually became dark yellow and then red-orange. After 8 h the solution was evaporated to dryness and was chromatographed on silica. Three compounds were isolated; eluting with toluene/n-hexane (1/3) gave $Ru_3(\mu_3\text{-NPh})(CO)_{10}$; that with toluene/n-hexane (1/1) gave $Ru_3(\mu\text{-DPPM})(CO)_{10}$ [9], and that with toluene gave $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$. The crude compound $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$ contains 0.5 mol of toluene of crystallisation: m.p. 148 °C (dec.), 50% yield.

Elemental analysis: Found: C, 48.6; H, 3.2; N, 1.6. $C_{38}H_{27}O_8NP_2Ru_3 \cdot 0.5$ toluene calcd.: C, 48.6; H, 3.1; N, 1.4%. IR: $\nu(CO) = 2067, 2014, 1999, 1963, 1682$ cm^{-1} in CH_2Cl_2. The ^{31}P NMR ($CDCl_3$) showed a singlet at 23.6 ppm. The ^1H NMR (CD_2Cl_2) showed a triplet at 3.11 ppm due to the coupling of CH_2 with two equivalent phosphorus atoms (J(P–H) 11.26 Hz).

Crystals suitable for the X-ray structure determination were obtained by slow diffusion of n-hexane into a benzene solution of the complex under dinitrogen.

Reactions with CO

General procedure. All reactions were carried out under high pressure in a glass-liner inside a stainless steel autoclave, equipped with a thermocouple to monitor the temperature of the solution during the reaction. The air in the autoclave was replaced by dinitrogen by three freeze-pump-thaw cycles, before the introduction of CO at the desired pressure. The autoclave was heated in an oil bath with magnetic stirring. At the end of the reaction the autoclave was cooled in an ice bath and pressure then released and the solution analysed by gas-chromatography.

The reaction was carried out with and without methanol present.

With MeOH. $Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$ (80 mg) was placed into the glass-liner and benzene (18 ml) and MeOH (2 ml) were added. The glass-liner was put in the autoclave and CO was introduced up to 60 atm by the procedure

Table 2

Crystal data and intensity collection parameters

Compound	$Ru_3(\mu_3\text{-NPh})(\mu\text{-DPPM})(CO)_8$
Formula	$C_{39}H_{27}NO_8P_2Ru_3$
F.W. (amu)	1002.81
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	14.027(7)
b (Å)	14.887(7)
c (Å)	18.499(9)
β (deg.)	93.52(4)
U (Å^3)	3856(6)
Z	4
D_{calcd} (g cm^{-3})	1.727
μ(Mo-K_α) (cm^{-1})	12.706
Min. transmission factor	0.91
Crystal dimensions (mm)	0.18 × 0.18 × 0.10
Scan mode	ω
ω-scan width (deg.)	$1.1 + 0.35 \tan \theta$
θ-range (deg.)	3 – 25
Octants of reciprocal space explored	$\pm h, +k, +l$
Measured reflections	6964
Unique observed reflections with I > 3σ(I)	5006
Final R and R_w indices [a]	0.022, 0.028
No. of variables	478
ESD [b]	1.050

[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$, $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{1/2}$. [b] $ESD = [\Sigma w(F_o - k|F_c|)^2/(NO - NV)]^{1/2}$.

Table 3

Fractional atomic coordinates for non-hydrogen atoms.

Atom	x	y	z
Ru(1)	−0.09970(2)	0.05296(2)	0.24627(1)
Ru(2)	0.08006(2)	0.13339(2)	0.25330(1)
Ru(3)	0.04349(2)	−0.01427(2)	0.16738(1)
C(11)	0.0385(3)	0.0018(2)	0.2853(2)
C(12)	−0.1483(3)	−0.0154(3)	0.3220(2)
C(13)	−0.2129(3)	0.0189(3)	0.1893(2)
C(21)	0.1552(3)	0.1316(2)	0.3420(2)
C(22)	0.1933(3)	0.1542(2)	0.2057(2)
C(31)	0.1277(3)	0.0045(3)	0.0896(2)
C(32)	−0.0550(3)	−0.0788(3)	0.1152(2)
C(33)	0.1119(3)	−0.1229(2)	0.1905(2)
O(11)	0.0620(2)	−0.0464(2)	0.3339(1)
O(12)	−0.1789(3)	−0.0575(2)	0.3665(2)
O(13)	−0.2818(2)	−0.0033(2)	0.1594(2)
O(21)	0.2017(2)	0.1270(2)	0.3944(2)
O(22)	0.2644(2)	0.1623(2)	0.1790(2)
O(31)	0.1755(2)	0.0121(2)	0.0431(2)
O(32)	−0.1139(2)	−0.1180(2)	0.0852(2)
O(33)	0.1543(2)	−0.1862(2)	0.2027(2)
P(1)	−0.15881(6)	0.18260(5)	0.29493(4)
P(2)	0.02338(6)	0.28312(5)	0.26596(4)
C	−0.1085(2)	0.2846(2)	0.2568(2)
N	−0.0201(2)	0.1110(2)	0.1683(1)
C(1)	−0.0438(2)	0.1638(2)	0.1056(2)
C(2)	−0.1379(3)	0.1795(3)	0.0817(2)
C(3)	−0.1599(3)	0.2322(3)	0.0209(2)
C(4)	−0.0893(3)	0.2684(3)	−0.0175(2)
C(5)	0.0038(3)	0.2546(3)	0.0059(2)
C(6)	0.0273(3)	0.2029(2)	0.0668(2)
C(111)	−0.1448(2)	0.1969(2)	0.3928(2)
C(112)	−0.0893(3)	0.1382(3)	0.4361(2)
C(113)	−0.0818(3)	0.1485(3)	0.5103(2)
C(114)	−0.1277(3)	0.2179(3)	0.5417(2)
C(115)	−0.1821(3)	0.2774(3)	0.4998(2)
C(116)	−0.1901(3)	0.2676(3)	0.4257(2)
C(121)	−0.2871(2)	0.1966(2)	0.2754(2)
C(122)	−0.3234(3)	0.2461(3)	0.2171(2)
C(123)	−0.4209(3)	0.2459(3)	0.1974(3)
C(124)	−0.4818(3)	0.1977(3)	0.2358(3)
C(125)	−0.4476(3)	0.1489(3)	0.2944(3)
C(126)	−0.3507(3)	0.1488(3)	0.3146(2)
C(211)	0.0535(2)	0.3511(2)	0.3467(2)
C(212)	0.0704(3)	0.3119(3)	0.4137(2)
C(213)	0.0923(3)	0.3648(3)	0.4745(2)
C(214)	0.0973(3)	0.4552(3)	0.4688(2)
C(215)	0.0809(4)	0.4950(3)	0.4036(3)
C(216)	0.0588(4)	0.4436(3)	0.3424(2)
C(221)	0.0562(2)	0.3596(2)	0.1942(2)
C(222)	0.1531(3)	0.3712(3)	0.1848(2)
C(223)	0.1842(3)	0.4284(3)	0.1325(3)
C(224)	0.1193(3)	0.4733(3)	0.0880(2)
C(225)	0.0232(3)	0.4632(3)	0.0964(2)
C(226)	−0.0091(3)	0.4062(2)	0.1489(2)

described above. The reaction was carried out at 170 °C for 5 h from the start of the heating. PhNHCOOMe was obtained in low yields, together with $Ru_3(\mu$-$DPPM)(CO)_{10}$ and $Ru_3(\mu_3$-$NPh)(\mu$-$DPPM)(CO)_8$, which were separated by column chromatography.

Without MeOH. The reaction was carried as described above, but without added MeOH (20 ml benzene). PhNCO and $PhNH_2$ were obtained in low yields, together with $Ru_3(\mu$-$DPPM)(CO)_{10}$ and $Ru_3(\mu_3$-$NPh)(\mu$-$DPPM)(CO)_8$.

X-ray data collection and structure determination

Crystal data and other experimental details are summarized in Table 2. The diffraction experiment was carried out on an Enraf–Nonius CAD-4 diffractometer at room temperature and using Mo-K_α radiation (λ 0.71073 Å). The calculations were performed on a PDP11/34 computer using the SDP-plus Structure Determination Package [10]. The diffracted intensities were corrected for Lorenz, polarization and absorption (empirical correction [11]). Anomalous dispersion corrections for atomic scattering factors of non-hydrogen atoms were taken from ref. 12. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares, minimizing the function $\Sigma w(F_o - k\,|\,F_c\,|)^2$. Weights assigned to individual observations were: $w = 1/\sigma\ (F_c)^2$ where $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_o\mathrm{Lp}$. Anisotropic thermal factors were refined for all the non-hydrogen atoms. All the phenyl hydrogens were introduced in the model at calculated position, but they were not refined. The final difference Fourier synthesis showed maxima residuals of 0.4 e/A^3. The atomic coordinates of the structure model are listed in Table 3. Tables of thermal parameters and lists of calculated structure factors are available from the authors.

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