the three P—O bonds [1.513 (5), 1.513 (5) and 1.519 (4) Å] lie between the values typical of single (1.75 Å) and double P—O (1.45 Å) bonds (see, for example, Zhang, Shao & Tang, 1990). To the best of our knowledge the ligand described in this study is the first example of a pyrazolone functionalized with a P-containing group.

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Structure of cis-Dicarbonyl[2-carboxylato-1-methoxycarbonyl-2-(4-methylphenyl)vinyl]-trans-bis(dimethylphenylphosphine)ruthenium(II), a Complex Containing a Bidentate Vinyl Ligand

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Abstract. $[Ru(CO)_2\{C(CO_2Me)\!=\!C(C\overline{O}O)(C_6H_4\text{-}Me)\}(PMe_2Ph)_2]$; $[Ru(C_{12}H_{10}O_4)(C_8H_{11}P)_2(CO)_2]$, $M_r = 651.6$, orthorhombic, $P2_12_12_1$, $a = 9.3667$ (8), $b = 13.6888$ (20), $c = 23.0421$ (20) Å, $V = 2954.4$ Å^3, $Z = 4$, $D_x = 1.465$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 5.74$ mm^{-1}, $F(000) = 1336$, $T = 298$ K, $R = 0.040$ for 4794 observed reflections with $F_o > 3\sigma(F_o)$ and 372 parameters. The complex exists as discrete monomeric units in the crystal, and exhibits approximate octahedral geometry around the Ru atom. The five-membered metallacycle ring is essentially planar with Ru—C and Ru—O distances of 2.087 (5) and 2.071 (4) Å. The Ru—C(carbonyl) distances of 1.824 (6) and 1.913 (6) Å show a marked difference. The average Ru—P distance is 2.384 (2) Å.

Introduction. Reactions between ruthenium(II) aryl complexes $[Ru(CO)_2(C_6H_4X\text{-}4)Cl(PMe_2Ph)_2]$ ($X = H$, Cl, Me or OMe) and the alkyne $MeO_2CC\!\equiv\!CCO_2Me$ yield vinyl complexes $[Ru(CO)_2\{C(CO_2Me)\!=\!C(CO_2Me)(C_6H_4X\text{-}4)\}Cl(PMe_2Ph)_2]$, assigned structure (I), where $L = PMe_2Ph$, corresponding to *cis* addition of the ruthenium–aryl bond to the alkyne (Crook, Chamberlain & Mawby, 1989). Apparent confirmation of this stereochemistry was provided by the thermal decomposition of the vinyl complexes in

CHCl$_3$ at 323 K, which gave products [$\overline{Ru(CO)_2}$-{C(CO$_2$Me)=C(CO$_2$Me)(C$_6$H$_3$X)}(PMe$_2$Ph)$_2$] of structure (II) by elimination of HCl (Crook, Giordano, Mawby, Reid & Reynolds, 1990).

(I)

(II)

(III)

(IV)
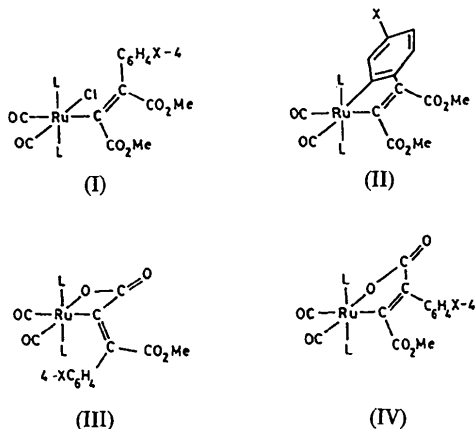
Each decomposition, however, yielded a second organometallic product as well, formed by elimination of MeCl from the corresponding vinyl complex. Two possible structures (III) and (IV), where L = PMe$_2$Ph, were proposed for these complexes. Given the stereochemistry (I) proposed for the precursor vinyl complexes, formation of (III), [$\overline{Ru(CO)_2}${C(C\overline{OO})=C(CO$_2$Me)(C$_6$H$_4$X)}(PMe$_2$Ph)$_2$], seemed logical, but the presence of the four-membered ring in (III) would make it very strained. In contrast, (IV), [$\overline{Ru(CO)_2}${C(CO$_2$Me)=C(C\overline{OO})-(C$_6$H$_4$X)}(PMe$_2$Ph)$_2$], would be less strained, but formation of (IV) from (I) can only be achieved by rearrangement of the vinyl ligand.

In order to determine whether the complexes possessed structure (III) or structure (IV), the product of thermal decomposition of [Ru(CO)$_2${C(CO$_2$Me)=C(CO$_2$Me)(C$_6$H$_4$Me-4)}Cl(PMe$_2$Ph)$_2$] was examined by X-ray diffraction.

Experimental. The preparation of the complex has been described previously (Crook *et al.*, 1989). Crystals suitable for X-ray analysis were obtained by slow recrystallization from a mixture of benzene and light petroleum. The crystal chosen for data collection measured 0.71 × 0.55 × 0.47 mm and was mounted with epoxy on a glass fibre. The orientation matrix was refined using ten centred reflections and reflection data were measured at room temperature on a Stadi-4 four-circle diffractometer using Ni-filtered Cu $K\alpha$ radiation. Accurate cell parameters were obtained from the 2θ values of 64 reflections measured at $\pm\omega$ (41 < 2θ < 45°). Data were collected in the range 4 < 2θ < 120° using the $\omega/2\theta$ scan mode, and were corrected for Lorentz, polarization and absorption effects. The range for h was −9 to

10, for k 0 to 15 and for l 0 to 25. The intensity variation over the period of data collection was less than 2%. Of the 5108 reflections measured, 5067 were unique and 4794 with $F_o > 3\sigma(F_o)$ were used in the refinement, $R_{int} = 0.020$.

A Patterson map revealed the position of the Ru atom. Refinement (on F^2) of Ru, followed by difference Fourier synthesis yielded the remaining non-H atoms. At isotropic convergence, final absorption corrections (minimum 0.789, maximum 1.494) were applied empirically using *DIFABS* (Walker & Stuart, 1983). Chemically reasonable positions for many H atoms were observed in difference maps after anisotropic refinement of all non-H atoms. The H atoms were placed at calculated positions near the observed electron density peaks and were given isotropic thermal factors derived from those of the parent atoms. The H atoms were included in the structure factor calculations but were not refined. Convergence was reached at $R = 0.040$, $wR = 0.045$ where $w = 1/\sigma^2(F_o)$. The enantiomeric structure gave $R = 0.062$ for the 3σ data set. A final difference map showed minimum and maximum residuals of -0.31 and 0.28 e Å^{-3}. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The largest shift/e.s.d. in the final refinement cycle was < 0.003, and unit weights were used.

Calculations were performed using the *SHELX76* system (Sheldrick, 1976) and Fig. 1 was drawn using the version of *ORTEP* contained in the *GX* crystallographic program system (Mallinson & Muir, 1985).

Discussion. The results of the structure determination show that the complex exists as discrete molecules,
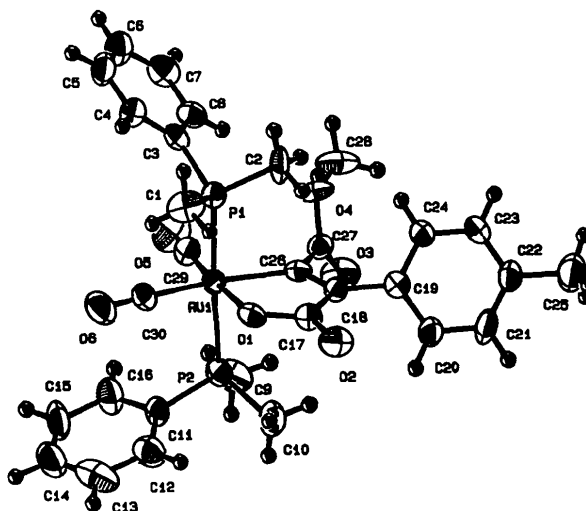

Fig. 1. A general view of the molecule (IV) showing the atom-labelling scheme.

and that it possesses structure (IV), [Ru̅(CO)₂{C-(CO₂Me)=C(COO)(C₆H₄Me-4)}(PMe₂Ph)₂]. Atomic coordinates and selected bond lengths and angles are listed in Tables 1 and 2.* The atom-numbering scheme and molecular structure are shown in Fig. 1.

There is slight distortion from octahedral geometry around the Ru atom. As in the case of [Ru̅-(CO)₂{C(CO₂Me)=C(CO₂Me)(C̅₆H₄)}(PMe₂Ph)₂] (Crook et al., 1990), the most notable departure results from the incorporation of the Ru atom into a five-membered ring. The angle O(1)—Ru—C(26) is 77.9 (2)°, close to the value of 77.5 (2)° for the corresponding C—Ru—C angle in [Ru̅(CO)₂-{C(CO₂Me)=C(CO₂Me)(C₆H₄)}(PMe₂Ph)₂]. The metallacycle (ring A) is essentially planar (r.m.s.d. from planarity = 0.0217 Å), and the remaining angles in the ring range from 114.8 (4) to 117.1 (3)°. The 4-methylphenyl group also contains a planar ring (ring B, r.m.s.d. from planarity = 0.0036 Å): interestingly, however, it is not coplanar with the metallacycle but is at an angle of 54.3° to it. The carboxylate group attached to C(26) is also twisted out of the plane of the metallacycle, again limiting the extent to which delocalization can occur.

The length of the bond from the metal to the sp^2-hybridized C atom C(26) [2.087 (5) Å] is within the range found in other ruthenium(II) complexes. It is slightly shorter than the corresponding bond in the complex [Ru̅(CO)₂{C(CO₂Me)=C(CO₂Me)(C̅₆H₄)}-(PMe₂Ph)₂] [2.099 (4) Å] (Crook et al., 1990), but longer than those found in two other complexes where the organic ligand is chelated to the metal through an O atom of a carboxylate group, [Ru̅{(CH=C(CO₂Bu)Me}H(PPh₃)₃] [2.061 (10) Å] (Komiya, Ito, Cowie, Yamamoto & Ibers, 1976) and [Ru̅{C(CO₂Me)=C(CO₂Me)H}{η⁵-C₅H₄C(CF₃)₂-OH}(PPh₃)] [2.035 (4) Å] (Raghavan & Davis, 1975).

The C=C bond [C(26)=C(18) 1.355 (7) Å] within the metallacycle is almost identical in length to that of the corresponding bond in [Ru̅(CO)₂{C(CO₂-Me)=C(CO₂Me)(C₆H₄)}(PMe₂Ph)₂] [1.352 (7) Å] (Crook et al., 1990), and is only slightly longer than the 'typical' double bond (1.33 Å).

There is a significant difference between the lengths of the bonds from the metal to the two carbonyl ligands [Ru—C(29) 1.824 (6), Ru—C(30) 1.913 (6) Å]. The bond to C(30) is presumably lengthened as a result of the trans effect of the organic ligand: it is comparable in length to the bonds to the equivalently placed carbonyl ligands in

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Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (Å²)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Ru	−0.14669 (4)	−0.03786 (3)	−0.11288 (2)	0.030
P(1)	−0.2623 (2)	−0.1764 (1)	−0.0714 (1)	0.034
P(2)	−0.0067 (2)	0.0954 (1)	−0.1473 (1)	0.040
C(1)	−0.1506 (8)	−0.2834 (5)	−0.0793 (3)	0.060
C(2)	−0.2950 (8)	−0.1750 (6)	0.0047 (3)	0.057
C(3)	−0.4329 (6)	−0.2112 (4)	−0.1016 (2)	0.037
C(4)	−0.4572 (7)	−0.3009 (5)	−0.1282 (3)	0.044
C(5)	−0.5893 (7)	−0.3232 (6)	−0.1518 (3)	0.055
C(6)	−0.6989 (7)	−0.2583 (5)	−0.1483 (3)	0.054
C(7)	−0.6783 (6)	−0.1707 (5)	−0.1203 (3)	0.057
C(8)	−0.5418 (6)	−0.1464 (5)	−0.0970 (3)	0.046
C(9)	−0.0974 (8)	0.2105 (5)	−0.1591 (4)	0.063
C(10)	0.1384 (8)	0.1320 (5)	−0.1000 (3)	0.062
C(11)	0.0747 (7)	0.0678 (4)	−0.2169 (3)	0.040
C(12)	0.2168 (7)	0.0356 (6)	−0.2207 (3)	0.060
C(13)	0.2712 (10)	0.0056 (6)	−0.2743 (4)	0.082
C(14)	0.1861 (9)	0.0047 (6)	−0.3225 (4)	0.070
C(15)	0.0490 (9)	0.0330 (7)	−0.3187 (3)	0.070
C(16)	−0.0086 (8)	0.0650 (5)	−0.2671 (3)	0.059
C(17)	0.0381 (5)	−0.0367 (5)	−0.0110 (2)	0.034
C(18)	−0.0824 (5)	0.0289 (4)	0.0058 (2)	0.031
C(19)	−0.0870 (6)	0.0735 (4)	0.0634 (2)	0.035
C(20)	0.0274 (7)	0.1279 (5)	0.0845 (3)	0.049
C(21)	0.0200 (8)	0.1715 (6)	0.1389 (2)	0.060
C(22)	−0.0971 (7)	0.1637 (5)	0.1733 (3)	0.045
C(23)	−0.2100 (7)	0.1103 (5)	0.1529 (3)	0.052
C(24)	−0.2055 (6)	0.0649 (5)	0.0989 (3)	0.046
C(25)	−0.0979 (10)	0.2106 (6)	0.2327 (3)	0.074
C(26)	−0.1817 (5)	0.0417 (4)	−0.0370 (2)	0.031
C(27)	−0.3003 (6)	0.1102 (4)	−0.0273 (3)	0.037
C(28)	−0.3466 (7)	0.1260 (7)	−0.0044 (4)	0.074
C(29)	−0.3029 (6)	0.0066 (4)	−0.1521 (3)	0.043
C(30)	−0.0851 (7)	−0.1192 (5)	−0.1756 (3)	0.040
O(1)	0.0251 (4)	−0.0794 (3)	−0.0619 (2)	0.037
O(2)	0.1442 (5)	−0.0489 (3)	0.0199 (2)	0.053
O(3)	−0.2904 (5)	0.1979 (3)	−0.0285 (2)	0.062
O(4)	−0.4242 (4)	0.0657 (3)	−0.0169 (2)	0.052
O(5)	−0.4057 (5)	0.0389 (5)	−0.1759 (2)	0.079
O(6)	−0.0441 (6)	−0.1684 (4)	−0.2127 (2)	0.068

Table 2. Selected bond lengths (Å) and angles (°)

Ru—P(1)	2.385 (2)	P(1)—Ru—P(2)	173.1 (1)
Ru—P(2)	2.383 (2)	P(1)—Ru—C(26)	90.4 (2)
Ru—O(1)	2.071 (4)	P(1)—Ru—C(29)	95.7 (2)
Ru—C(26)	2.087 (5)	P(1)—Ru—C(30)	88.7 (2)
Ru—C(29)	1.824 (6)	P(2)—Ru—C(26)	88.1 (2)
Ru—C(30)	1.913 (6)	P(2)—Ru—C(29)	91.2 (3)
P(1)—C(1)	1.808 (6)	P(2)—Ru—C(30)	91.6 (3)
P(1)—C(2)	1.780 (6)	C(26)—Ru—C(29)	96.6 (4)
P(1)—C(3)	1.806 (6)	C(26)—Ru—C(30)	169.9 (2)
P(2)—C(9)	1.811 (7)	C(29)—Ru—C(30)	93.5 (3)
P(2)—C(10)	1.812 (7)	O(1)—Ru—P(1)	84.7 (1)
P(2)—C(11)	1.815 (6)	O(1)—Ru—P(2)	88.4 (1)
C(3)—C(4)	1.392 (8)	O(1)—Ru—C(26)	77.9 (2)
C(4)—C(5)	1.385 (9)		
C(5)—C(6)	1.359 (10)	O(1)—Ru—C(29)	174.4 (2)
C(6)—C(7)	1.376 (10)	O(1)—Ru—C(30)	92.0 (2)
C(7)—C(8)	1.373 (9)	O(1)—C(17)—C(18)	114.8 (4)
C(3)—C(8)	1.401 (8)	O(2)—C(17)—C(18)	123.3 (5)
C(11)—C(12)	1.404 (9)	O(2)—C(17)—O(1)	121.9 (5)
C(12)—C(13)	1.398 (11)	C(18)—C(26)—Ru	115.1 (4)
C(13)—C(14)	1.367 (12)	C(27)—C(26)—Ru	125.4 (4)
C(14)—C(15)	1.344 (11)	O(3)—C(27)—C(26)	125.0 (6)
C(15)—C(16)	1.377 (10)	O(4)—C(27)—C(26)	113.2 (5)
C(11)—C(16)	1.396 (9)	O(4)—C(27)—O(3)	121.8 (6)
O(1)—C(17)	1.317 (7)	O(5)—C(29)—Ru	177.0 (6)
O(2)—C(17)	1.235 (6)	O(6)—C(30)—Ru	178.0 (6)
O(3)—C(27)	1.205 (7)	C(19)—C(18)—C(17)	119.8 (5)
O(4)—C(27)	1.333 (7)	C(26)—C(18)—C(17)	114.9 (5)
O(4)—C(28)	1.442 (8)	C(26)—C(18)—C(19)	125.2 (5)
O(5)—C(29)	1.193 (7)	C(20)—C(19)—C(18)	121.1 (5)
O(6)—C(30)	1.154 (7)	C(25)—C(22)—C(21)	120.0 (6)
C(17)—C(18)	1.488 (8)	C(25)—C(22)—C(23)	122.3 (6)
C(18)—C(19)	1.477 (8)		
C(19)—C(20)	1.392 (8)	Phenyl rings (average angles)	
C(26)—C(27)	1.470 (8)	C(3)—C(8)	119.98
C(22)—C(25)	1.511 (9)	C(11)—C(16)	119.98
		C(19)—C(24)	119.97

$[\overline{Ru}(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4)\}(PMe_2-Ph)_2]$ [1.914 (5) Å] (Crook et al., 1990) and [Ru-$(CO)_2\{C(CO_2Me)=C(CO_2Me)Cl\}Cl(PMe_2Ph)_2]$ [1.91 (2) Å] (Holland, Howard & Mawby, 1983). For the latter complex, this increased length of the Ru—CO bond is reflected in the lability of the carbonyl ligand towards substitution.

The Ru—P bond lengths are equal to within expected error [2.385 (2) and 2.383 (2) Å] but are significantly longer than those in $[\overline{Ru}(CO)_2\{C-\overline{(CO_2Me)=C(CO_2Me)(C_6H_4)}\}(PMe_2Ph)_2]$ [2.362 (1) and 2.364 (1) Å] (Crook et al., 1990).

The packing in the crystal is largely stabilized by van der Waals forces. There are five intermolecular contacts of less than 3.5 Å between non-H atoms. Four of these are with the molecule which is related by the symmetry operations $0.5 + x$, $0.5 - y$, $-z$. The contacts are: $O(2)\cdots C(1)$ 3.291; $O(2)\cdots C(4)$ 3.368; $O(3)\cdots C(28)$ 3.406; $O(3)\cdots C(20)$ 3.203 Å. The other contact is with the molecule symmetry-related by $0.5 - x$, $-y$, $0.5 + z$, and is $C(25)\cdots C(4)$ 3.475 Å. The closest contact between H atoms is $H(301)\cdots H(302)$ (2.262 Å) to the molecule related by $0.5 + x$, $0.5 - y$, $-z$.

There remains the question as to how the complexes (IV) are formed. It is clear from the NMR spectra of the vinyl complexes $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)(C_6H_4X-4)\}Cl(PMe_2Ph)_2]$ that they are produced from $[Ru(CO)_2(C_6H_4X-4)Cl(PMe_2Ph)_2]$ and $MeO_2CC\equiv CCO_2Me$ in a single isomeric form, but it is also evident that *one* of their decomposition pathways [either to (II) or to (IV)] must involve a rearrangement of the vinyl ligand. One possibility is that, under the conditions used for

the thermal decompositions, rotation can occur about the C=C double bond of the vinyl ligand. This bond is unexpectedly long [1.41 (3) Å] in the related complex $[Ru(CO)_2\{C(CO_2Me)=C(CO_2Me)-Cl\}Cl(PMe_2Ph)_2]$, suggesting that resonance structure (IB), where $L = PMe_2Ph$ and $Y = Cl$ or C_6H_4X-4, may make a significant contribution to the bonding in these vinyl complexes, reducing the bond order and the barrier to rotation about the C=C bond.

(IA)   (IB)
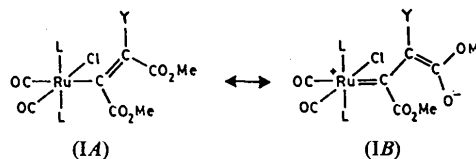
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Structure of Bis(4-aminobenzenesulfonato-O)heptaaquaneodymium 4-Aminobenzenesulfonate Hydrate

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Abstract. $[Nd(C_6H_6NO_3S)_2(H_2O)_7][C_6H_6NO_3S].H_2O$, $M_r = 804.9$, orthorhombic, *Pcab*, $a = 32.017$ (9), $b = 23.557$ (7), $c = 7.933$ (3) Å, $V = 5983$ (4) Å³, $Z = 8$, $D_m = 1.78$, $D_x = 1.787$ (1) Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 15.3$ mm⁻¹, $F(000) = 3256$, $T = 303$ (1) K, final $R = 0.054$ for 3935 reflections. The Nd ions are surrounded by seven water molecules and two 4-aminobenzenesulfonate anions.

Introduction. This work reports the structure of neodymium 4-aminobenzenesulfonate. Our interest in this complex ensues from our general interest in lanthanide complexes with N-donor ligands.

Experimental. The title compound was prepared by adding freshly precipitated neodymium hydroxide to a hot aqueous solution of 4-aminobenzenesulfonic