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XXVI *. AN UNUSUAL BINUCLEAR COMPLEX OBTAINED FROM $Ru_3(CO)_{10}(sp)$ ($sp = 2\text{-}CH_2CHC_6H_4PPh_2$): ISOLATION AND X-RAY STRUCTURE OF $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$

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Summary

Minor products of the pyrolysis (80°C, 30 min) of $Ru_3(CO)_{10}(sp)$ ($sp = 2\text{-}CH_2{=}CHC_6H_4PPh_2$) have been identified as $Ru_3(CO)_{12}$ and the binuclear complex $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$ (A); the major product is $H_2Ru_3(\mu\text{-}\eta^2,P\text{-}HC_2C_6H_4PPh_2)(CO)_8$, which can subsequently be converted into a mixture of $Ru_3(CO)_{12}$ and A at 80°C under CO (5 atm). An X-ray study of A (monoclinic, space group *Cc*, *a* 36.294(15), *b* 15.183(9), *c* 15.724(6) Å, *β* 115.93°, $Z = 12$; 3617 data with $I > 2\sigma(I)$ refined to $R = 0.056$, $R_w = 0.059$) showed the presence of an $MeCC_6H_4PPh_2$ ligand bridging an $Ru_2(CO)_6$ group by an η^3-benzylic group to one Ru, the exocyclic carbon forming a σ-bond to the second Ru.

Introduction

We have recently described the electron transfer-catalysed reaction between $Ru_3(CO)_{12}$ and the olefinic tertiary phosphine, $2\text{-}CH_2{=}CHC_6H_4PPh_2$ (sp), which affords $Ru_3(\mu\text{-}\eta^2,P\text{-}CH_2{=}CHC_6H_4PPh_2)(CO)_{10}$ (I) and the conversion of I to the hydrido cluster $H_2Ru_3(\mu\text{-}\eta^2,P\text{-}HCCC_6H_4PPh_2)(CO)_8$ (II) under mild conditions [1]. A later account reported the further dehydrogenation of II in a reaction with $Ru_3(CO)_{12}$ to give $Ru_4(\mu_4\text{-}HC_2C_6H_4PPh_2)(CO)_{11}$ (III) (Scheme 1) [2]. In their original account of the thermal reactions between $Ru_3(CO)_{12}$ and sp, Bennett and coworkers [3] described the formation of $Ru(CO)_3(sp)$ and $Ru(CO)_2(sp)_2$ (in reflux-

* For Part XXV, see ref. 2.

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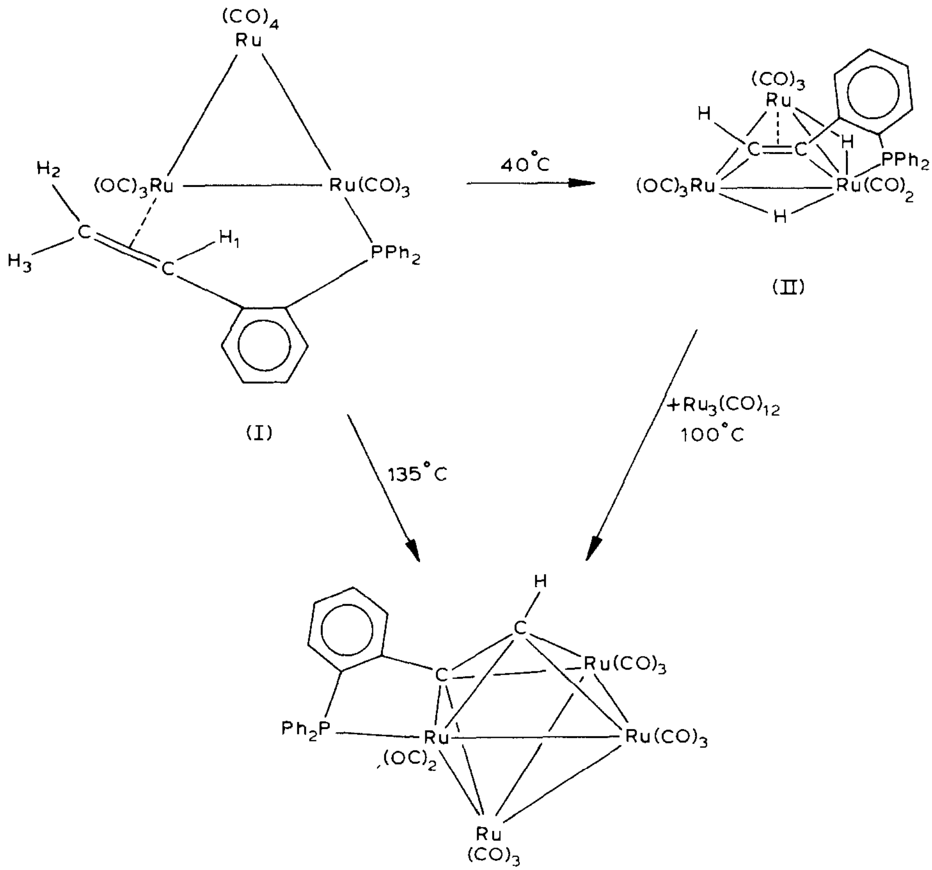
TABLE 1

POSITIONAL PARAMETERS FOR $Ru_2(CO)_6[PPh_2(C_6H_4CCH_3)]$

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	x/b	z/c
Ru(11)	0.7681	0.1497	0.8482	Ru(21)	0.9305	0.3669	0.3264	Ru(31)	0.0341	0.0989	0.5801
	0.0000	0.0001	0.0000		0.0001	0.0001	0.0002		0.0001	0.0001	0.0002
Ru(12)	0.8298	0.0604	0.9986	Ru(22)	0.8723	0.4624	0.1765	Ru(32)	0.0483	−0.0572	0.6831
	0.0001	0.0001	0.0002								
P(11)	0.7368	0.0680	0.9241		0.0001	0.0001	0.0002		0.0001	0.0001	0.0002
	0.0002	0.0004	0.0005	P(21)	0.9659	0.4400	0.2543	P(31)	0.1051	0.0756	0.6474
C(111)	0.7241	0.1441	0.7264		0.0002	0.0005	0.0005		0.0002	0.0005	0.0005
	0.0009	0.0018	0.0023	C(211)	0.9728	0.3632	0.4513	C(311)	0.0304	0.1552	0.4681
O(111)	0.6999	0.1388	0.6494		0.0008	0.0017	0.0020		0.0008	0.0019	0.0021
	0.0008	0.0016	0.0019	O(211)	1.0018	0.3619	0.5236	O(311)	0.0303	0.1876	0.4023
C(112)	0.7579	0.2639	0.8872		0.0006	0.0013	0.0016		0.0006	0.0015	0.0015
	0.0009	0.0021	0.0021	C(212)	0.9362	0.2522	0.2892	C(312)	0.0357	0.1976	0.6610
O(112)	0.7509	0.3320	0.9033		0.0008	0.0018	0.0020		0.0010	0.0024	0.0024
	0.0008	0.0018	0.0018	O(212)	0.9379	0.1779	0.2684	O(312)	0.0379	0.2537	0.7116
C(113)	0.8039	0.2030	0.8075		0.0006	0.0013	0.0014		0.0008	0.0020	0.0020
	0.0010	0.0021	0.0023	C(213)	0.8924	0.3189	0.3641	C(313)	−0.0220	0.0950	0.5358
O(113)	0.8248	0.2427	0.7815		0.0009	0.0020	0.0021		0.0009	0.0018	0.0019
	0.0007	0.0014	0.0015	O(213)	0.8667	0.2938	0.3860	O(313)	−0.0587	0.1000	0.4981
C(121)	0.8676	0.1099	0.9670		0.0008	0.0018	0.0018		0.0008	0018	0.0019
	0.0010	0.0023	0.0024	C(221)	0.8280	0.4193	0.1896	C(321)	−0.0052	−0.0649	0.6579
O(121)	0.8940	0.1363	0.9496		0.0012	0.0025	0.0027		0.0009	0.0019	0.0021
	0.0009	0.0018	0.0020	O(221)	0.8017	0.3917	0.2118	O(321)	−0.0411	−0.0697	0.6412
C(122)	0.8353	0.1399	1.0971		0.0009	0.0019	0.0021		0.0007	0.0015	0.0017
	0.0010	0.0022	0.0025	C(222)	0.8672	0.3860	0.0832	C(322)	0.0623	−0.0025	0.8031
O(122)	0.8405	0.1832	1.1613		0.0009	0.0022	0.0023		0.0008	0.0022	0.0021
	0.0007	0.0015	0.0017	O(222)	0.8601	0.3303	0.0217	O(322)	0.0680	0.0279	0.8753
C(123)	0.8680	−0.0227	1.0864		0.0007	0.0015	0.0017		0.0007	0.0017	0.0019
	0.0012	0.0028	0.0029	C(223)	0.8400	0.5437	0.0986	C(323)	0.0589	−0.1790	0.7296
O(123)	0.8903	−0.0766	1.1307		0.0012	0.0025	0.0028		0.0009	0.0023	0.0022
	0.0009	0.0020	0.0020	O(223)	0.8171	0.5938	0.0374	O(323)	0.0667	−0.2474	0.7540
C(11)	0.7717	−0.0236	0.9673		0.0011	0.0026	0.0027		0.0006	0.0016	0.0016
	0.0007	0.0016	0.0018	C(21)	0.9321	0.5362	0.2099	C(31)	0.1041	−0.0405	0.6532
C(12)	0.7722	−0.0840	1.0344		0.0007	0.0016	0.0018		0.0007	0.0015	0.0016

C(13)	0.7881	−0.1722	1.0376								
	0.0008	0.0019	0.0020	C(23)	0.9255	0.6862	0.1419	C(33)	0.1451	−0.1807	0.6813
C(14)	0.8006	−0.1969	0.9668		0.0008	0.0019	0.0020		0.0009	0.0021	0.0022
	0.0008	0.0018	0.0019	C(24)	0.9136	0.7136	0.2164	C(34)	0.1147	−0.2178	0.5959
C(15)	0.8025	−0.1371	0.9047		0.0009	0.0022	0.0023		0.0008	0.0020	0.0020
	0.0009	0.0019	0.0021	C(25)	0.9070	0.6574	0.2713	C(35)	0.0779	−0.1688	0.5448
C(16)	0.7889	−0.0433	0.9029		0.0008	0.0018	0.0020		0.0009	0.0019	0.0020
	0.0008	0.0017	0.0018	C(26)	0.9150	0.5642	0.2720	C(36)	0.0718	−0.0787	0.5757
C(17)	0.7953	0.0219	0.8508		0.0008	0.0018	0.0020		0.0008	−0.0314	0.5309
	0.0007	0.0016	0.0017	C(27)	0.9087	0.4946	0.3265	C(37)	0.0331	−0.0314	0.5309
C(18)	0.8135	−0.0013	0.7859		0.0007	0.0018	0.0019		0.0007	0.0016	0.0017
	0.0007	0.0017	0.0017	C(28)	0.8922	0.5281	0.4028	C(38)	−0.0019	−0.0726	0.4459
C(141)	0.7271	0.1084	1.0234		0.0009	0.0021	0.0022		0.0010	0.0021	0.0023
	0.0005	0.0011	0.0010	C(241)	0.9752	0.3973	0.1562	C(341)	0.1411	0.1173	0.7628
C(142)	0.7029	0.0576	1.0530		0.0005	0.0011	0.0011		0.0005	0.0013	0.0011
	0.0005	0.0011	0.0010	C(242)	1.0004	0.4461	0.1275	C(342)	0.1828	0.1149	0.7850
C(143)	0.6969	0.0838	1.1312		0.0005	0.0011	0.0011		0.0005	0.0013	0.0011
	0.0005	0.0011	0.0010	C(243)	1.0088	0.4154	0.0543	C(343)	0.2116	0.1448	0.8729
C(144)	0.7153	0.1608	1.1797		0.0005	0.0011	0.0011		0.0005	0.0013	0.0011
	0.0005	0.0011	0.0010	C(244)	0.9921	0.3358	0.0097	C(344)	0.1987	0.1772	0.9386
C(145)	0.7395	0.2115	1.1501		0.0005	0.0011	0.0011		0.0005	0.0013	0.0011
	0.0005	0.0011	0.0010	C(245)	0.9669	0.2871	0.0383	C(345)	0.1571	0.1796	0.9163
C(146)	0.7455	0.1853	1.0719		0.0005	0.0011	0.0011		0.0005	0.0013	0.0011
	0.0005	0.0011	0.0010	C(246)	0.9585	0.3178	0.1115	C(346)	0.1283	0.1497	0.8284
C(151)	0.6866	0.0197	0.8507		0.0005	0.0011	0.0011		0.0005	0.0013	0.0011
	0.0004	0.0011	0.0012	C(251)	1.0164	0.4848	0.3345	C(351)	0.1297	0.1040	0.5729
C(152)	0.6798	−0.0709	0.8396		0.0004	0.0010	0.0011		0.0005	0.0011	0.0012
	0.0004	0.0011	0.0012	C(252)	1.0471	0.4257	0.3892	C(352)	0.1483	0.0419	0.5391
C(153)	0.6411	−0.1030	0.7790		0.0004	0.0010	0.0011		0.0005	0.0011	0.0012
	0.0004	0.0011	0.0012	C(253)	1.0860	0.4568	0.4498	C(353)	0.1650	0.0677	0.4781
C(154)	0.6092	−0.0444	0.7294		0.0004	0.0010	0.0011		0.0005	0.0011	0.0012
	0.0004	0.0011	0.0012	C(254)	1.0942	0.5469	0.4557	C(354)	0.1630	0.1557	0.4510
C(155)	0.6160	0.0462	0.7405		0.0004	0.0010	0.0011		0.0005	0.0011	0.0012
	0.0004	0.0011	0.0012	C(255)	1.0635	0.6060	0.4010	C(355)	0.1444	0.2179	0.4849
C(156)	0.6547	0.0782	0.8011		0.0004	0.0010	0.0011		0.0005	0.0011	0.0012
	0.0004	0.0011	0.0012	C(256)	1.0246	0.5749	0.3404	C(356)	0.1277	0.1920	0.5458
					0.0004	0.0010	0.0011		0.0005	0.0011	0.0012

SCHEME 1



(I) (II) (III)

ing octane), and $Ru(CO)(sp)_2$, $Ru(CO)_2[Ph_2PC_6H_4CH(CH_2)_2CHC_6H_4PPh_2]$ and $Ru(CO)(Ph_2PC_6H_4CH{=}CHCH{=}CHC_6H_4PPh_2)$ (in refluxing nonane). Further investigation of the thermal rearrangements of I has shown that in refluxing cyclohexane, small amounts of a new yellow, binuclear complex characterised as $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$ (IV), and the subject of this paper, can be isolated.

Experimental

Pyrolysis of $Ru_3(CO)_{10}(sp)$

A solution of $Ru_3(CO)_{10}(sp)$ (100 mg, 0.12 mmol) was heated in refluxing cyclohexane (20 ml) for 30 min, after which time the reaction was adjudged complete (the disappearance of the $\nu(CO)$ band at 2094 cm^{-1} was monitored). Evaporation and preparative TLC (silica gel, cyclohexane) gave three products: (i) $Ru_3(CO)_{12}$ (4 mg, 5%); (ii) yellow $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$ (IV) (6 mg, 8%) from CH_2Cl_2/MeOH, m.p. 103–108°C (Found: C, 48.18; H, 2.55. $C_{26}H_{19}O_2PRu_2$ calcd.: C, 47.28; H, 2.90%). Infrared (cyclohexane); $\nu(CO)$ at 2069s, 2048(sh), 2037s, 2004s, 1991vs, 1982s cm^{-1}. ^1H NMR ($CDCl_3$): δ (ppm) 3.10, d, $J(CP)$ 1.5 Hz, 3H, CH_3;

6.44–8.02, m, 14H, aromatic. Mass spectrum (70 eV): $[M - Me - nCO]^+$ ($n = 0$–6) at m/e 647, 619, 591, 563, 535, 507, 479. (iii) yellow $H_2Ru_3(\mu\text{-}\eta^2,P\text{-}HCCC_6H_4PPh_2)(CO)_8$ (II), (61 mg, 65%) identified from its IR spectrum. Three purple products were also present in trace amounts only.

Pyrolysis of $H_2Ru_3(\mu_3\text{-}P,\eta^2\text{-}HCCC_6H_4PPh_2)(CO)_8$ under CO

A solution of II (50 mg, 0.061 mmol) in cyclohexane (30 ml) was heated in an autoclave (80°C, 2 h) under CO (5 atm). Solvent was removed and the residue chromatographed (silica gel, eluting with hexane) to give three bands: (1) $Ru_3(CO)_{12}$ (22 mg, 56%); (ii) $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$ (IV), (10 mg, 25%); and (iii) unreacted starting material (6 mg, 12%) all identified by comparison of infrared spectra with authentic samples.

Crystal Structure of $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}PPh_2C_6H_4CCH_3)(CO)_6$

A yellow crystal of dimensions 0.6 × 0.15 × 0.08 mm was used to obtain cell dimensions and intensity data on a Nicolet P3 diffractometer, using graphite monochromated Mo-K_α radiation.

Crystal Data: $C_{26}H_{19}O_6PRu_2$, $M = 660.55$, monoclinic, space group Cc; a

TABLE 2

BOND LENGTHS FOR $Ru_2(CO)_6[Ph_2P(C_6H_4CCH_3)]$ (Å)

	Molecule 1	Molecule 2	Molecule 3
Ru(1)–Ru(2)	2.796(3)	2.786(3)	2.789(3)
Ru(1)–P	2.334(6)	2.336(7)	2.343(7)
Ru(1)–C(7)	2.17(2)	2.09(3)	2.12(2)
Ru(2)–C(1)	2.33(2)	2.29(2)	2.28(2)
Ru(2)–C(6)	2.23(2)	2.24(3)	2.22(3)
Ru(2)–C(7)	2.18(2)	2.20(3)	2.12(2)
P–C(1)	1.80(2)	1.84(3)	1.77(2)
P–C(41)	1.85(1)	1.84(1)	1.83(1)
P–C(51)	1.83(1)	1.84(1)	1.81(1)
C(1)–C(2)	1.39(4)	1.50(4)	1.51(3)
C(1)–C(6)	1.43(3)	1.43(4)	1.39(3)
C(2)–C(3)	1.45(4)	1.36(4)	1.42(4)
C(3)–C(4)	1.43(4)	1.47(4)	1.43(4)
C(4)–C(5)	1.36(4)	1.31(4)	1.43(4)
C(5)–C(6)	1.50(4)	1.44(4)	1.50(4)
C(6)–C(7)	1.37(3)	1.44(4)	1.46(3)
C(7)–C(8)	1.48(3)	1.64(4)	1.52(4)
Ru(1)–C(11)	1.88(3)	1.89(3)	1.91(3)
Ru(1)–C(12)	1.93(3)	1.88(3)	1.95(4)
Ru(1)–C(13)	1.87(3)	1.87(3)	1.84(3)
Ru(2)–C(21)	1.82(4)	1.83(4)	1.81(3)
Ru(2)–C(22)	1.91(3)	1.81(3)	1.92(3)
Ru(2)–C(23)	1.94(4)	1.77(4)	1.96(4)
C(11)–O(11)	1.15(3)	1.16(3)	1.15(3)
C(12)–O(12)	1.12(3)	1.18(3)	1.15(3)
C(13)–O(13)	1.17(3)	1.19(3)	1.20(3)
C(21)–O(21)	1.17(3)	1.23(4)	1.21(3)
C(22)–O(22)	1.15(3)	1.22(3)	1.16(3)
C(23)–O(23)	1.15(4)	1.22(4)	1.10(3)

36.294(15), b 15.183(9), c 15.724(6) Å, β 115.93°, U 7794 Å^3, D_m 1.67 g cm^{-3}, D_c 1.68 g cm^{-3} for $Z = 12$; $F(000) = 3888$, μ(Mo-K_α) 12.4 cm^{-1}, λ(Mo-K_α) 0.7107 Å.

Intensity data were collected in the range $3° < 2\theta < 42°$ to give a total of 3813 unique reflections which were corrected for absorption using the azimuthal scan method (maximum and minimum transmission factors were 0.891 and 0.766, respectively). The 3617 reflections for which $I > 2\sigma(I)$ were used in all calculations.

The structure was solved by direct methods (SHELX) to locate the positions of the Ru atoms, with all other non-hydrogen atoms being located in subsequent difference fourier calculations. In the final cycle of full-matrix least-squares refinement the Ru and P atoms were assigned anisotropic temperature factors while other atoms were treated isotropically. The unsubstituted phenyl rings were refined as rigid groups, but hydrogen atoms were not included. The refinement converged at

TABLE 3

SELECTED BOND ANGLES FOR $Ru_2(CO)_6[PPh_2(C_6H_4CCH_3)]$

	Molecule 1	Molecule 2	Molecule 3
Ru(2)–Ru(1)–P	72.5(2)	73.5(2)	73.8(2)
Ru(2)–Ru(1)–C(7)	50.2(6)	51.1(7)	52.2(6)
Ru(2)–Ru(1)–C(11)	147.9(9)	149.8(8)	146.9(8)
Ru(2)–Ru(1)–C(12)	111.2(9)	111.4(8)	109.2(1)
Ru(2)–Ru(1)–C(13)	94.6(10)	94.6(9)	94.9(9)
P–Ru(1)–C(7)	80.4(6)	81.3(7)	82.2(6)
Ru(1)–Ru(2)–C(1)	76.7(6)	76.7(6)	75.0(6)
Ru(1)–Ru(2)–C(6)	73.8(7)	75.3(7)	73.6(7)
Ru(1)–Ru(2)–C(7)	49.8(6)	47.9(7)	48.3(6)
Ru(1)–Ru(2)–C(21)	89.4(11)	95.5(12)	91.1(10)
Ru(1)–Ru(2)–C(22)	98.1(10)	97.1(10)	96.0(10)
Ru(1)–Ru(2)–C(23)	168.1(12)	167.0(12)	166.6(9)
C(1)–Ru(2)–C(6)	36.6(9)	36.9(9)	36.0(8)
C(1)–Ru(2)–C(7)	65.3(6)	65.2(9)	65.6(8)
C(6)–Ru(2)–C(7)	36.1(9)	37.9(10)	38.0(9)
Ru(1)–P–C(1)	100.5(8)	98.2(8)	97.5(8)
Ru(1)–P–C(41)	124.8(6)	125.7(6)	124.4(7)
Ru(1)–P–C(51)	117.6(6)	116.0(6)	115.3(7)
P–C(1)–C(2)	124.6(19)	123.3(19)	122.1(18)
P–C(1)–C(6)	110.3(18)	113.2(19)	113.4(17)
P–C(1)–Ru(2)	94.6(10)	96.1(10)	99.3(10)
C(2)–C(1)–C(6)	122 (2)	120 (2)	120 (2)
C(1)–C(2)–C(3)	120 (2)	120 (2)	119 (2)
C(2)–C(3)–C(4)	118 (2)	117 (3)	122 (3)
C(3)–C(4)–C(5)	121 (2)	123 (3)	118 (3)
C(4)–C(5)–C(6)	122 (2)	123 (3)	122 (3)
C(5)–C(6)–C(1)	115 (2)	116 (2)	118 (2)
C(1)–C(6)–C(7)	121 (2)	115 (2)	119 (2)
C(5)–C(6)–C(7)	124 (2)	130 (3)	123 (2)
C(6)–C(1)–Ru(2)	68.2(14)	69.6(14)	69.7(14)
C(1)–C(6)–Ru(2)	75.2(15)	73.5(15)	74.3(14)
C(6)–C(7)–C(8)	119 (2)	114 (2)	119 (2)
C(6)–C(7)–Ru(1)	117.6(17)	121.4(19)	115.1(16)
C(6)–C(7)–Ru(2)	74.1(14)	72.6(15)	70.3(14)
Ru(1)–C(7)–Ru(2)	80.0(8)	81.0(9)	79.4(8)

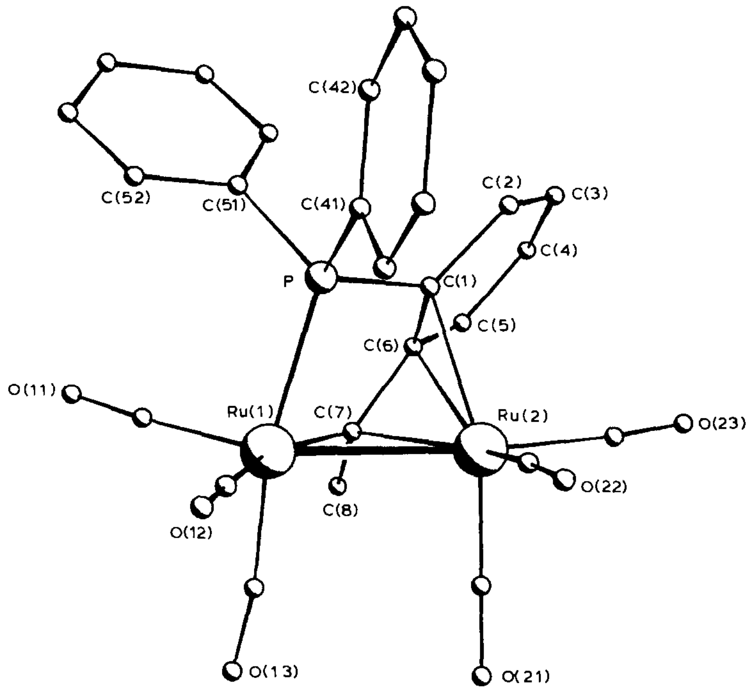


Fig. 1. A view of one of the independent molecules of $Ru_2(\mu\text{-}\eta^1,\eta^3\text{-}MeCC_6H_4PPh_2)(CO)_6$ showing atom labelling.

$R = 0.056$, $R_w = 0.059$ where $w = 1.0015(\sigma^2(F) + 0.00253\ F^2)^{-1}$. A final difference map showed no residual peaks greater than 0.6 $e\text{Å}^{-3}$.

Atomic coordinates are listed in Table 1, and selected bond distances and angles are given in Tables 2 and 3. The molecular structure is illustrated in Figure 1. Lists of thermal parameters and structure factors are available on request from the authors.

Results and discussions

The relatively pale colour and simple IR spectrum in the ν(CO) region suggested that IV was a complex of low nuclearity. This was confirmed by the mass spectrum, which contained ions $[M - Me - nCO]^+$ ($n = 0$–6), where $M = Ru_2(CO)_6(sp)$. However, the ^1H NMR spectrum contained only two resonances, a doublet at δ 3.1 ppm and a complex well-resolved multiplet between δ 6.4–8.0 ppm, of relative intensities 3/14. Considering the origin of the phosphine ligand, and the ready loss of a CH_3 group from the molecular ion, it was reasonable to assign the former signal to a CH_3 group coupled to the ^{31}P nucleus: evidently the original vinyl group had isomerised, probably to a CMe function. This was confirmed by an X-ray structural determination, which also enabled a rationalisation of the broad, finely-structure aromatic resonance.

The asymmetric unit contains three independent molecules, two the same and the third an enantiomer (the mirror plane associated with the c-glide of space group Cc

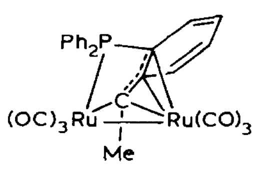
means equal numbers of enantiomers are in the unit cell). The structural parameters of individual molecules do not differ significantly so the following discussion is based on average values.

Each molecule consists of two $Ru(CO)_3$ groups connected by a Ru–Ru bond (2.790 Å) which is bridged by the rearranged sp ligand. This is coordinated to Ru(1) by the phosphorus atom, and to Ru(2) by an η^3-allylic interaction involving C(1), C(6) and C(7); C(7) is also η^1-bonded to Ru(1). Each ruthenium atom has approximately octahedral coordination, and has a formal 18 electron count, each of the metal atoms also being ligated by three CO groups. An alternative interpretation is in terms of C(7) acting as a bridging methylene carbon atom and the C(1)–C(6) bond coordinated via a two-electron π-donor interaction to Ru(2). The distances between Ru(2) and the three coordinated carbon atoms are more closely similar than in other η^3-benzyl complexes. Thus the difference between the Ru–C(1) and Ru–C(7) bonds is only 0.13 Å, whereas the equivalent distances are 0.37 Å in (η^3-$CH_2C_6H_5$)$Co[P(OMe)_3]_3$ [4], 0.21 Å in (η^3-$CH_2C_6H_4CH_3$)$Mo(CO)_2Cp$ [5], 0.36 Å in [η^3-$(CH_3C_6H_4)_2C$]$Mo_2(CO)_4Cp_2$ [6] and 0.43 Å in [PtW(η^3-CHC_6H_4Me-4)$(CO)_2(PMe_3)_2(Cp)]^+$ [7]. This indicates a strong interaction between Ru(2) and the ring carbon atoms. The phenyl ring is essentially planar (maximum deviation from the least-squares plane is 0.07 Å); the exocyclic C(7) is twisted out of this plane by 0.18 Å while the P is displaced by 0.8 Å from the plane in the opposite sense. Averaged over all three independent molecules, the C(1)–C(6), C(2)–C(3) and C(4)–C(5) bonds are shorter than the other bonds in the ring suggesting that coordination of this group has localised the π-electron density in one of the valence-bond resonance forms of the benzene ring, although individual differences are not crystallographically significant.

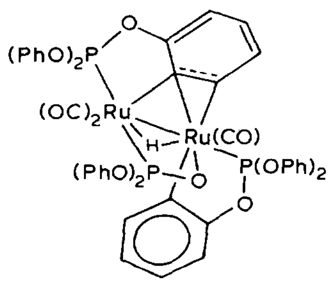
The C(6)–C(7) bond (1.42 Å) is indicative of a bond order less than one, consistent with the π-allyl bonding model. Similarly the C(6)–C(7)–C(8) angle of 117° is also consistent with the expected sp^2 hybridisation at C(7).

The chelating mode of the phosphine ligand is apparently quite strained since the angles around P atom differ markedly from tetrahedral values; the Ru(1)–P–C(1) value of 99° is particularly low while that to the free phenyl ring Ru(1)–P–C(41) at 124° is high.

Complex IV is probably an intermediate in the breakdown of the cluster complexes to the mononuclear products described earlier. It is not possible to say how the isomerisation of the vinyl to the ethylidene ligand occurs, but a plausible route from (1) is via the hydrido complex II (Scheme 2). Transfer of both cluster-bound

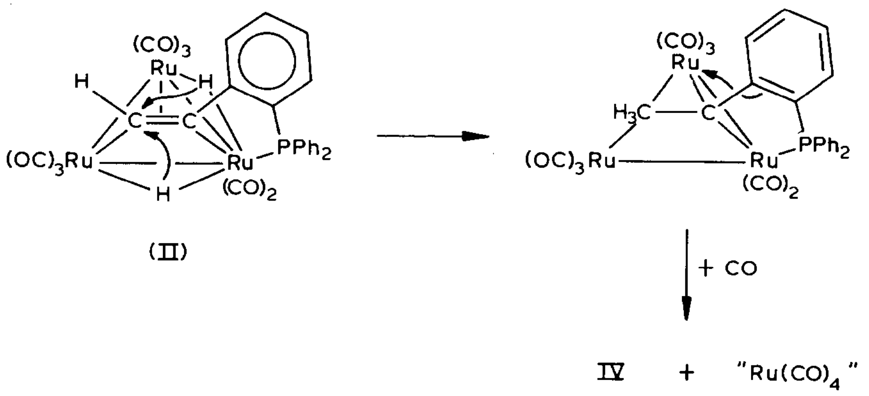


(IV)



(V)

SCHEME 2



hydrogens to the terminal (β) carbon of the C_2 unit would afford the ligand found in IV; the C_6H_4 ring is then ideally located for interaction of its π system with Ru. A similar situation is found in $HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$ (V), obtained by controlled pyrolysis of $Ru_3(CO)_9[P(OPh)_3]_3$, although in this example, there is no exocyclic carbon to generate an η^3 interaction [8]. Formation of IV is completed by addition of CO and extrusion of an $Ru(CO)_4$ fragment; trimerisation of this would give $Ru_3(CO)_{12}$, which is isolated in yields comparable with that of IV. In a separate experiment it was shown that under CO pressure II is converted to IV in 25% yield, with $Ru_3(CO)_{12}$ as the other product. This strongly implicates the intermediacy of II in the overall pyrolysis of $Ru_3(CO)_{10}(sp)$ to IV. It is interesting to note that the presence of $Ru_3(CO)_{12}$ was found to be necessary for the conversion of II to III; the formation of III in the thermal decomposition of I, free of $Ru_3(CO)_{12}$, may result from the presence of small smounts of $Ru_3(CO)_{12}$ generated by the breakdown of I or II to IV.

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References

1 M.I. Bruce, B.K. Nicholson and M.L. Williams, J. Organomet. Chem., 243 (1983) 69.
2 M.I. Bruce, E. Horn, M.R. Snow and M.L. Williams, J. Organomet. Chem., 255 (1983) 255.
3 M.A. Bennett, R.N. Johnson and I.B. Tomkins, J. Am. Chem. Soc., 96 (1974) 61.
4 J.R. Blecke, R.R. Burch, C.L. Coulman and B.C. Schardt, Inorg. Chem., 20 (1981) 1316.
5 F.A. Cotton and M.D. La Prade, J. Am. Chem. Soc., 90 (1968) 5418.
6 L. Messerle and M.D. Curtis, J. Am. Chem. Soc., 102 (1980) 7789.
7 J.C. Jeffery, I. Moore, H. Razay and F.G.A. Stone, J. Chem. Soc. Chem. Comm., (1981) 1255.
8 M.I. Bruce, J. Howard, I.W. Nowell, G. Shaw and P. Woodward, J. Chem. Soc., Chem. Comm., (1972) 1041; M.I. Bruce, G. Shaw and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1973) 1667.