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PHOSPHIDO-BRIDGED MIXED METAL COMPLEXES. REACTION OF $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ WITH BIS(DIPHENYLPHOSPHINO)METHANE (dppm): SYNTHESIS AND CRYSTAL STRUCTURES OF HETEROBIMETALLIC (Ru–Co) COMPOUNDS WITH CHELATING AND BRIDGING dppm LIGANDS *

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Summary

The reaction of $(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**1**) with $Ph_2PCH_2PPh_2$ (dppm) in THF gave the dppm chelate complex $(dppm)(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**3**) at 40 °C but the dppm-bridged complex $(OC)_3Ru(\mu\text{-}dppm)(\mu\text{-}PPh_2)Co(CO)_2$ (**4**) at reflux. Treatment of **1** with Me_3NO at −55 °C in the presence of dppm gave the dppm monodentate derivative $(dppm)(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**2**) which contained two isomers with a relative *cis* or *trans* position of the dppm ligand with respect to the phosphido bridge. The structures of **2**, **3** and **4** are based on a ^{31}P NMR study and on X-ray diffraction studies of **3** and **4**. It is shown that complexes **3** and **4** do not undergo interconversion, and are formed from **2** by competitive intramolecular carbonyl displacement reactions.

Introduction

Although the phosphido (PR_2) group has several attractive features as a ligand for polynuclear chemistry [1], including the ability to form strong bonds to group VIII elements and the flexibility to bridge both bonding and non-bonding metals, there are now numerous examples in which reaction, involving the $M(\mu\text{-}PR_2)M$

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* Dedicated to Professor Jean Tirouflet on the occasion of his retirement, as a mark of admiration for his contribution to chemistry and for his enthusiasm.

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moiety, leads either to fragmentation [2] or conversion of the μ-PR_2 group to another ligand [3]. Despite the non-innocent behaviour of the μ-PR_2 group in some instances, many novel transformations have been accomplished on phosphido-bridged compounds [4] and it is clear that cleavage of a M–M bond by two-electron addition with retention of the PR_2 bridge is an intrinsically useful property of many phosphido systems. In attempting to exploit the chemistry of mixed metal μ-PR_2 complexes we were intrigued by the possibility of retaining the desirable features of the $M-PR_2-M$ system while simultaneously enhancing resistance to fragmentation and increasing the electron density at the metal centres. An appropriate bridging ligand for this purpose is bis(diphenylphosphino)methane (dppm) [5]. In this paper we describe the synthesis and characterization of the μ-PPh_2, μ-dppm-bridged ruthenium–cobalt compound $(OC)_3Ru(\mu\text{-}PPh_2)(\mu\text{-dppm})Co(CO)_2$ (**4**). The formation of **4** from $(OC)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**1**) which is accompanied by that of the dppm chelate $(dppm)(OC)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**3**), proceeds via the monodentate dppm complex $(dppm)(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**2**). The interconversions between **2**, **3** and **4** are described as are the X-ray crystal structures of **3** and **4**. A preliminary account of part of this work has been published [6].

Experimental

General procedures

Standard techniques, involving Schlenk type equipment, were used for the manipulation of air-sensitive compounds under a blanket of nitrogen. All solvents were dried (over sodium benzophenone ketyl, for THF, and ether, over CaH_2 for hexane and benzene, and over P_2O_5 for CH_2Cl_2) and saturated with nitrogen prior to use. For chromatographic separations on thick layer plates Merck silica-gel was used.

Instrumentation

Infrared spectra were recorded on Perkin–Elmer 457 and 180 instruments using either Nujol mulls or cyclohexane solutions in matched 0.5-mm NaCl cells. ^1H and ^{31}P NMR spectra were recorded on Bruker WP-80 spectrometers operating at 80 MHz for ^1H and 32.38 MHz for ^{31}P at the Centre de Mesures Physiques de l'Ouest, Université de Rennes. ^{31}P spectra were proton-noise decoupled, and shifts are reported relative to external 85% H_3PO_4. ^1H shifts are relative to Me_4Si. Microanalyses were carried out by the CNRS, Villeurbanne laboratory (France).

Ligand position assignments are based on the Ru(μ-P)Co plane which is arbitrarily regarded as the equatorial plane. The *cis* and *trans* positions at the Ru center are then specified with respect to the phosphido group.

Preparation of $(dppm)(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ (2)

To a solution of light red **1** [1e,7] (0.2 g, 0.369 mmol) in THF (30 ml) in a 100 ml Schlenk tube at −55 °C were added successively one equivalent of dppm (0.37 mmol, 0.14 g) and one equivalent of dry sublimed Me_3NO (0.37 mmol, 28 mg). The mixture was stirred at −55 °C and analyzed by thin layer chromatography on silica-gel (eluant: hexane/ether). After 12 h at −55 °C the solvent was evaporated under vacuum. The residue was dissolved in 5 ml of dichloromethane and the solution passed through a 5 cm silica-gel column under nitrogen (eluant:

hexane/ether). The solution was concentrated to 5 ml and cooled and the red-orange precipitate of **2** was isolated (0.22 g, 66.4%). IR (C_6H_{12}): 2070 w, 1999 vs, 1979 m, 1944 m cm^{-1}. $^{31}P\ \{^1H\}$ NMR (32.38 MHz, 193 K, CD_2Cl_2), δ (ppm) **2**-*trans*: 184.90 (d, μ-PPh_2, $^2J(P_\mu-P_{trans})$ 104.6 Hz), 24.30 (dd, CH_2PPh_2Ru) and −27.60 (d, Ph_2PCH_2); $^2J(P_{Ru}-P)$ 115.1 Hz; **2**-*cis*: 172.25 (s, μ-PPh_2), 29.64 (d, $-CH_2PPh_2Ru$) and −28.40 (d, Ph_2PCH_2), $^2J(P_{Ru}-P)$ 104.6 Hz). ^1H NMR (80 MHz, 309 K, $CDCl_3$) δ (ppm): 3.56 (broad signal, CH_2 (**2**-*cis*, **2**-*trans*). Anal. Found: C, 57.60; H, 3.59; P, 10.35. $C_{43}H_{32}CoO_6P_3Ru$ calc.: C, 57.53; H, 3.73; P, 10.48.

Preparation of (dppm)(OC)$_2$Ru(μ-PPh$_2$)Co(CO)$_3$ (3)

Method A (from 1). A solution of **1** [1e,7] (1 mmol, 0.54 g) and of one equivalent of dppm (0.39 g) in 60 ml of THF was kept at 40 ° C. Monitoring by thin layer chromatography and IR spectroscopy showed the disappearance of **1** and the growth of two dark red complexes. After 12 h at 40 ° C, the major product, which migrated the faster on thin layer chromatography, was obtained (0.2 g; 23%) by concentration of the solution and chromatography on a 30 cm column of silica gel (eluant: hexane/ether (9/1)) and recrystallization from hexane/dichloromethane, IR of **3** (C_6H_{12}): 2019 s, 1985 vs, 1952 m, 1939 m, 1934 m, 1913 w. ^1H NMR ($CDCl_3$, 303 K, 60 MHz), δ (ppm) 7.9–7.1 (m, Ph), 4.70 (t, CH_2, $^2J(PH)$ 10 Hz); $^{31}P\ \{^1H\}$ NMR (CD_2Cl_2, 223 K, 32.38 MHz), δ (ppm) 187.33 (dd, μ-PPh_2), −12.47 (dd, Ru-PPh_2(*trans*)), −29.02 (dd, Ru-PPh_2(*cis*); $^2J(P_\mu-P(trans))$ 131.8, $^2J(P_\mu-P(cis)$ 22.0, $^2J(P(cis)-P(trans))$ 43.9 Hz.

Method B (from 2). A solution of 0.22 mmol (0.2 g) of **2** was dissolved in 30 ml of THF in a Schlenk tube was stirred at room temperature and the reaction monitored by thin layer chromatography on silica-gel (eluant: hexane/ether) and by infra-red spectroscopy. After 3 d at 20 ° C the IR spectrum remained unchanged. The solution was then passed through a 5 cm column of silica-gel (eluant: dichloromethane/hexane). The solvent was evaporated and the products were dissolved in 20 ml of dichloromethane/hexane (10/90). The solution was kept at 5 ° C and the dark red crystals of **3** (62 mg; 32%) obtained were filtered off. The remaining solution was then concentrated to 5 ml and kept at 5 ° C to afford 18 mg (9.4%) of red crystals of **4**.

Preparation of (OC)$_3$Ru(μ-dppm)(μ-PPh$_2$)Co(CO)$_2$ (4)

Method A (from 1). A solution of 1 mmol (0.54 g) of **1** and 1 mmol of dppm (0.39 g) in 60 ml of THF was stirred under reflux for 10 h, after which the IR spectrum indicated that complex **4** was the major product. Chromatography on a 30 cm column of silica-gel (eluant: hexane/ether (9/1)) and recrystallization of the product from in dichloromethane/hexane, afforded 0.55 g of **4** (63%). IR of **4** (C_6H_{12}): 2046 w, 1984 s, 1956 vs, 1907 m cm^{-1}. ^1H NMR ($CDCl_3$, 303 K, 250 MHz) δ (ppm): 7.77–7.13 (m, Ph), 4.48 (t, CH_2, $^2J(P-H)$ 10.2 Hz); $^{31}P\ \{^1H\}$ NMR ($CDCl_3$, 223 K, 32.38 MHz), δ (ppm): 203.5 (dd, μ-PPh_2), 47.4 (dd, Co-PPh_2), 24.3 (dd, Ru-PPh_2); $^2J(P\mu-P_{Ru})$ 92.8, $^2J(P_{Co}-P_{Ru})$ 78.0, $^2J(P\mu-P_{Co})$ 107.4 Hz.

Method B (from 2). Complex **2** (0.2 g, 0.22 mmol) was dissolved in 30 ml of THF, previously heated at 50 ° C contained in a Schlenk tube. The solution was stirred at 50 ° C for 6 h. IR monitoring indicated that **3** was formed as a minor product and **4** as the major product. The solution was passed through a 5 cm column of silica-gel (eluant hexane/ether). Evaporation of the solvent left a red oil, which was dissolved in a dichloromethane/hexane mixture from which only complex **4** crystallized in 45% yield (87 mg).

X-ray structural analysis of (dppm)(OC)$_2$Ru(μ-PPh$_2$)Co(CO)$_3$ (3) and of (OC)$_3$Ru(μ-dppm)(μ-PPh$_2$)Co(CO)$_2$ (4)

Crystals were attached to a eucentric goniometer head, and mounted on a Syntex P2$_1$ diffractometer for preliminary examination. Fifteen strong reflections well dispersed in reciprocal space were selected, and a least-squares fit of the angular settings used to derive unit cell dimensions by the Syntex autoindexing and cell refinement procedures. Both complexes crystallize in monoclinic space groups as shown in Table 1. A systematic check of absences confirmed the space group assignments, $P2_1/c$ for **3** and $P2_1/n$ for **4**. Intensity data were collected at 293 ± 1 K using graphite-monochromated Mo-K_α radiation with θ–2θ scans. Data were corrected for Lorentz and polarization effects but not for absorption.

TABLE 1

CRYSTAL DATA, INTENSITY COLLECTION, REDUCTION, AND REFINEMENT FOR (dppm)(OC)$_2$Ru(μ-PPh$_2$)Co(CO)$_3$ (3) AND (OC)$_3$Ru(μ-dppm)(μ-PPh$_2$)Co(CO)$_2$ (4)

	3	**4**
Formula	$RuCoP_3O_5C_{42}H_{32}$	$RuCoP_3O_5C_{42}H_{32}$
Mol.wt.	869.64	869.64
Cryst. class	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (Å)	16.398(2)	11.590(1)
b (Å)	11.239(1)	27.458(4)
c (Å)	21.182(2)	12.620(2)
β (°)	90.68(1)	101.54(1)
V (Å^3)	3903.5(7)	3935.0(9)
Z	4	4
ρ_{measd} (g cm^{-3})	1.47	1.47
ρ_{calcd} (g cm^{-3})	1.480	1.468
$F(000)$	1760	1760
μ(Mo-K_α) (cm^{-1})	9.88 cm^{-1}	9.80 cm^{-1}
T (K)	293±1	293±1
Cryst. size (mm)	0.28×0.32×0.32	0.14×0.15×0.21
Transmission factors	0.68–0.80	0.79–0.81
Radiatn	λ (0.71069 Å)	λ (0.71069 Å)
Max 2Θ (deg)	48	42
Scan speed (deg min^{-1})	2.93–29.30	2.55–29.30
Scan width (deg)	0.8° below K_{α_1} to 0.8° above K_{α_2}	0.75 below K_{α_1} to 0.075 above K_{α_2}
Stds (every 100 measurmts)	900,008	010.0; 400
Variance of stds	±2%	−4%
Reflctns measd	6158	4250
Reflctns obsd ($I \geqslant 3\sigma(I)$)	4115	2918
R (isotropic)	0.079	0.068
R (anisotropic)	0.043	0.049
Final R	0.033	0.037
R_w	0.037	0.041
ω^{-1}	$1.6–0.009\|F_0\|+0.00015\|F_0\|^2$	$1.5–0.017\|F_0\|+0.00014\|F_0\|^2$
Max. residuals (e Å^{-3})	0.4	0.46

TABLE 2

ATOMIC POSITIONAL PARAMETERS (fractional $\times 10^4$) FOR (dppm)$(CO)_2$Ru(μ-PPh_2)Co$(CO)_3$ (3) [a]

Atom	*x*	*y*	*z*
Ru	2281.3(2)	2613.3(3)	1892.8(2)
Co	2204.5(4)	2663.0(6)	578.6(3)
P(1)	3286.9(7)	2926.1(10)	1156.7(5)
P(2)	2259.6(7)	458.0(10)	2015.2(5)
P(3)	1010.9(7)	2026.6(10)	2309.5(5)
O(1)	3318(3)	3102(4)	3046(2)
O(2)	1764(3)	5188(3)	1817(2)
O(3)	913(2)	910(3)	713(2)
O(4)	1459(3)	4890(3)	168(2)
O(5)	2936(3)	1642(5)	−524(2)
C(1)	2902(3)	2880(4)	2627(2)
C(2)	1974(3)	4220(4)	1826(2)
C(3)	1427(3)	1600(4)	693(2)
C(4)	1765(3)	4051(5)	355(2)
C(5)	2651(4)	2045(6)	−91(2)
C(6)	1175(3)	417(4)	2251(2)
C(7)	4162(3)	1917(4)	1138(2)
C(8)	4607(3)	1801(5)	589(3)
C(9)	5254(4)	1013(6)	566(3)
C(10)	5460(4)	332(6)	1074(4)
C(11)	5032(4)	433(5)	1619(3)
C(12)	4385(3)	1234(4)	1657(2)
C(13)	3810(3)	4372(4)	1151(2)
C(14A)	3996(6)	4817(9)	555(5)
C(14B)	3581(11)	5305(15)	759(10)
C(15A)	4406(7)	5928(9)	535(5)
C(15B)	4028(14)	6448(17)	816(14)
C(16A)	4634(8)	6482(8)	1087(6)
C(16B)	4698(18)	6711(28)	1234(17)
C(17A)	4441(7)	6037(10)	1639(6)
C(17B)	4927(10)	5634(14)	1601(9)
C(18A)	4041(6)	4934(8)	1686(4)
C(18B)	4483(10)	4545(13)	1567(7)
C(19)	2809(3)	−195(2)	2688(2)
C(20)	3332(3)	−1150(4)	2615(3)
C(21)	3745(4)	−1589(7)	3151(4)
C(22)	3637(5)	−1082(8)	3729(4)
C(23)	3114(4)	−147(7)	3797(3)
C(24)	2706(3)	291(5)	3282(2)
C(25)	2337(3)	−654(4)	1398(2)
C(26)	2801(3)	−467(5)	875(3)
C(27)	2791(5)	−1283(6)	382(3)
C(28)	2348(5)	−2316(5)	433(3)
C(29)	1875(4)	−2499(5)	941(3)
C(30)	1863(3)	−1679(4)	1424(2)
C(31)	26(2)	2324(4)	1925(2)
C(32)	−29(3)	3069(5)	1413(2)
C(33)	−780(4)	3253(6)	1119(3)
C(34)	−1460(3)	2706(6)	1339(3)
C(35)	−1415(3)	1980(6)	1855(3)
C(36)	−668(3)	1784(5)	2151(2)

continued

TABLE 2 (continued)

Atom	x	y	z
C(37)	788(2)	2377(5)	3126(2)
C(38)	480(3)	1553(6)	3552(2)
C(39)	243(4)	1930(8)	4152(3)
C(40)	306(4)	3083(9)	4317(3)
C(41)	625(4)	3911(7)	3913(3)
C(42)	873(3)	3547(5)	3318(3)

[a] Occupancy: $A = 2/3$; $B = 1/3$.

The heavy-atom positions were located by Patterson syntheses and all other non-hydrogen atoms via Fourier maps phased with these heavy atoms. R values ($R = \Sigma \| F_0 | - | F_c \| / \Sigma F_0$ at various stages in the refinements are given in Table 1. One phenyl ring in **3** was found to exhibit two-fold disorder. In final cycles of refinement a model with occupancy factors of $2/3:1/3$ provided a satisfactory fit. Following two cycles of anisotropic refinement, difference Fourier syntheses allowed location of all hydrogen atoms except those of the disordered phenyl group in **3**. Those located were included and refined isotropically. The final R and R_w ($R_w = [\Sigma w[| F_0 | - | F_c |]^2 / w | F_0 |^2]^{1/2}$ values were 0.033 and 0.037 for **3**, and 0.037 and 0.041 for **4**, respectively, where the function minimized was $\Sigma w(| F_0 | - | F_c |)^2$. Scattering factors used were taken from ref. 8. Corrections for the real and imaginary components of anomalous scattering were included for Ru and Co. Computations were carried out on IBM 4341 systems in the University of Waterloo Computing Centre using programs described elsewhere [9]. Tables 2 and 3 list atomic positions for **3** and **4** respectively. A selection of bond lengths and angles is given in Table 4 for **3** and in Table 5 for **4**. Perspective views of **3** and **4** are shown in the Figs. 1 and 2 respectively. Tables of thermal parameters additional bond lengths and angles, and lists of structure factors are available from the authors.

Results and discussion

Synthesis

Site selectivity in substitution reactions and the influence of one metal centre on the reactivity patterns of the other are key aspects of heterobimetallic chemistry [10]. The readily accessible and air-stable phosphido-bridged Ru–Co complex $(CO)_4Ru(\mu\text{-}PPh_2)Co(CO)_3$ (**1**) [1e] is a strikingly simple molecule with which to probe fundamental concepts of binuclear complex reactivity since it contains two metals, with differing affinities for small molecules (e.g. H_2 and alkynes) [11] linked together via a single phosphido bridge and a strong metal–metal interaction. This system might be expected to permit electronic interaction between the metal centres. We have already examined the behaviour of **1** towards carbonyl substitution with a variety of monodentate phosphines [10]. Monosubstitution appears to take place exclusively at the ruthenium site, to give a mixture of two isomers differing in respect of the position of the phosphine equatorially *cis* or *trans* to the phosphido bridge. Relative equatorial and axial positions are specified with respect to the equatorial $Ru(\mu\text{-}P)Co$ plane and *cis* and *trans* positions with respect to the phosphido bridge. With basic phosphines, such as PMe_3 or PMe_2Ph, disubstitution

TABLE 3

ATOMIC POSITIONS (fractional $\times 10^4$) FOR $(CO)_3Ru(\mu\text{-dppm})(\mu\text{-PPh}_2)Co(CO)_2$ (4)

Atom	*x*	*y*	*z*
Ru	2410.0(5)	959.6(2)	2298.3(4)
Co	2318.5(7)	1842.7(3)	3319.7(7)
P(1)	1956.8(15)	1147.5(6)	3957.1(13)
P(2)	2836.5(15)	1292.2(6)	696.7(13)
P(3)	3015.7(14)	2205.8(6)	2049.7(13)
O(1)	2328(7)	−133(2)	1959(5)
O(2)	−195(5)	1135(3)	1281(5)
O(3)	4991(4)	972(2)	3499(4)
O(4)	51(5)	2322(2)	2974(5)
O(5)	3763(5)	2325(2)	5149(4)
C(1)	2371(7)	279(3)	2087(6)
C(2)	766(7)	1076(3)	1673(6)
C(3)	4034(6)	980(2)	3045(5)
C(4)	915(6)	2114(2)	3058(6)
C(5)	3229(6)	2113(3)	4419(5)
C(6)	2524(5)	1953(2)	674(5)
C(7)	2863(5)	881(2)	5185(5)
C(8)	3384(7)	432(3)	5170(6)
C(9)	4044(8)	235(3)	6116(8)
C(10)	4150(7)	486(4)	7050(7)
C(11)	3665(7)	935(4)	7097(6)
C(12)	3000(7)	1133(3)	6143(6)
C(13)	498(5)	994(2)	4182(4)
C(14)	−150(6)	1331(2)	4636(5)
C(15)	−1258(6)	1217(3)	4827(6)
C(16)	−1725(6)	767(3)	4549(6)
C(17)	−1110(8)	428(3)	4105(7)
C(18)	4(7)	545(3)	3920(7)
C(19)	1917(5)	1074(2)	−573(5)
C(20)	1740(8)	580(3)	−692(6)
C(21)	1075(9)	398(3)	−1659(7)
C(22)	615(7)	710(3)	−2475(6)
C(23)	769(6)	1199(3)	−2366(5)
C(24)	1444(6)	1379(2)	−1412(5)
C(25)	4312(6)	1218(3)	430(5)
C(26)	4782(7)	1535(3)	−224(6)
C(27)	5893(9)	1451(4)	−452(9)
C(28)	6505(9)	1047(5)	−43(10)
C(29)	6049(10)	713(5)	572(10)
C(30)	4937(9)	806(4)	809(8)
C(31)	2526(5)	2840(2)	1866(5)
C(32)	3136(6)	3189(2)	2549(6)
C(33)	2757(6)	3668(2)	2502(6)
C(34)	1744(7)	3801(2)	1770(6)
C(35)	1132(6)	3451(3)	1097(6)
C(36)	1517(6)	2975(2)	1156(6)
C(37)	4592(5)	2277(2)	2123(5)
C(38)	5022(6)	2518(2)	1311(6)
C(39)	6203(6)	2554(3)	1331(7)
C(40)	7007(6)	2359(3)	2180(7)
C(41)	6612(6)	2135(3)	3002(6)
C(42)	5407(6)	2089(3)	2988(5)

TABLE 4

MAIN BOND LENGTHS (Å) AND ANGLES (°) IN (dppm)(CO)$_2$Ru(μ-PPh$_2$)Co(CO)$_3$ (3)

Ru–Co	2.7858(7)	Ru–P(1)	2.310(1)
Ru–P(2)	2.437(1)	Ru–P(3)	2.366(1)
Ru–C(1)	1.873(5)	Ru–C(2)	1.880(5)
Co–P(1)	2.165(1)	Co–C(3)	1.766(5)
Co–C(4)	1.779(5)	Co–C(5)	1.749(6)
P(1)–C(7)	1.830(4)	P(1)–C(13)	1.838(4)
P(2)–C(6)	1.853(4)	P(2)–C(19)	1.830(5)
P(2)–C(25)	1.814(4)	P(3)–C(6)	1.833(4)
P(3)–C(31)	1.830(4)	P(3)–C(37)	1.815(4)
C(1)–O(1)	1.140(6)	C(2)–O(2)	1.141(6)
C(3)–O(3)	1.147(6)	C(4)–O(4)	1.138(7)
C(5)–O(5)	1.129(8)	P(2)$\cdots$P(3)	2.778(2)
Co–Ru–P(1)	49.19(3)	Co–Ru–P(2)	97.22(2)
Co–Ru–P(3)	110.42(3)	Co–Ru–C(1)	147.6(2)
Co–Ru–C(2)	84.1(2)	P(1)–Ru–P(2)	103.57(3)
P(1)–Ru–P(3)	158.92(3)	P(1)–Ru–C(1)	98.7(2)
P(1)–Ru–C(2)	89.8(2)	P(2)–Ru–P(3)	70.68(3)
P(2)–Ru–C(1)	94.5(2)	P(2)–Ru–C(2)	163.5(2)
P(3)–Ru–C(1)	102.0(2)	P(3)–Ru–C(2)	93.4(2)
C(1)–Ru–C(2)	92.9(2)		
Ru–Co–P(1)	53.87(3)	Ru–Co–C(3)	82.8(2)
Ru–Co–C(4)	107.2(2)	Ru–Co–C(5)	142.0(2)
P(1)–Co–C(3)	127.1(2)	P(1)–Co–C(4)	110.9(2)
P(1)–Co–C(5)	99.5(2)	C(3)–Co–C(4)	109.8(2)
C(3)–Co–C(5)	98.8(3)	C(4)–Co–C(5)	107.8(3)
Ru–P(1)–Co	76.93(3)	Ru–P(1)–C(7)	119.1(1)
Ru–P(1)–C(13)	118.5(1)	Co–P(1)–C(7)	122.8(1)
Co–P(1)–C(13)	119.8(1)	C(7)–P(1)–C(13)	100.4(2)
Ru–P(2)–C(6)	93.9(1)	Ru–P(2)–C(19)	118.3(1)
Ru–P(2)–C(25)	127.4(1)	C(6)–P(2)–C(19)	104.2(2)
C(6)–P(2)–C(25)	104.6(2)	C(19)–P(2)–C(25)	104.3(2)
Ru–P(3)–C(6)	96.8(1)	Ru–P(3)–C(31)	124.0(1)
Ru–P(3)–C(37)	118.9(1)	C(6)–P(3)–C(31)	106.3(2)
C(6)–P(3)–C(37)	108.1(2)	C(31)–P(3)–C(37)	101.4(2)
Ru–C(1)–O(1)	174.5(2)	Ru–C(2)–O(2)	176.1(2)
Co–C(3)–O(3)	174.2(2)	Co–C(4)–O(4)	174.2(2)
Co–C(5)–O(5)	179.6(3)	P(2)–C(6)–P(3)	97.8(1)

predominates with both ligands located on the ruthenium atom. Although exhaustive studies were not carried out, substitution at the cobalt site was observed in only one instance, with trimethylphosphite P(OMe)$_3$ [10b], and then only following disubstitution at the ruthenium atom. In view of these results it was of interest to examine the behaviour of **1** toward bidentate ligands with a propensity to bridge rather than chelate. Such a ligand is dppm [5].

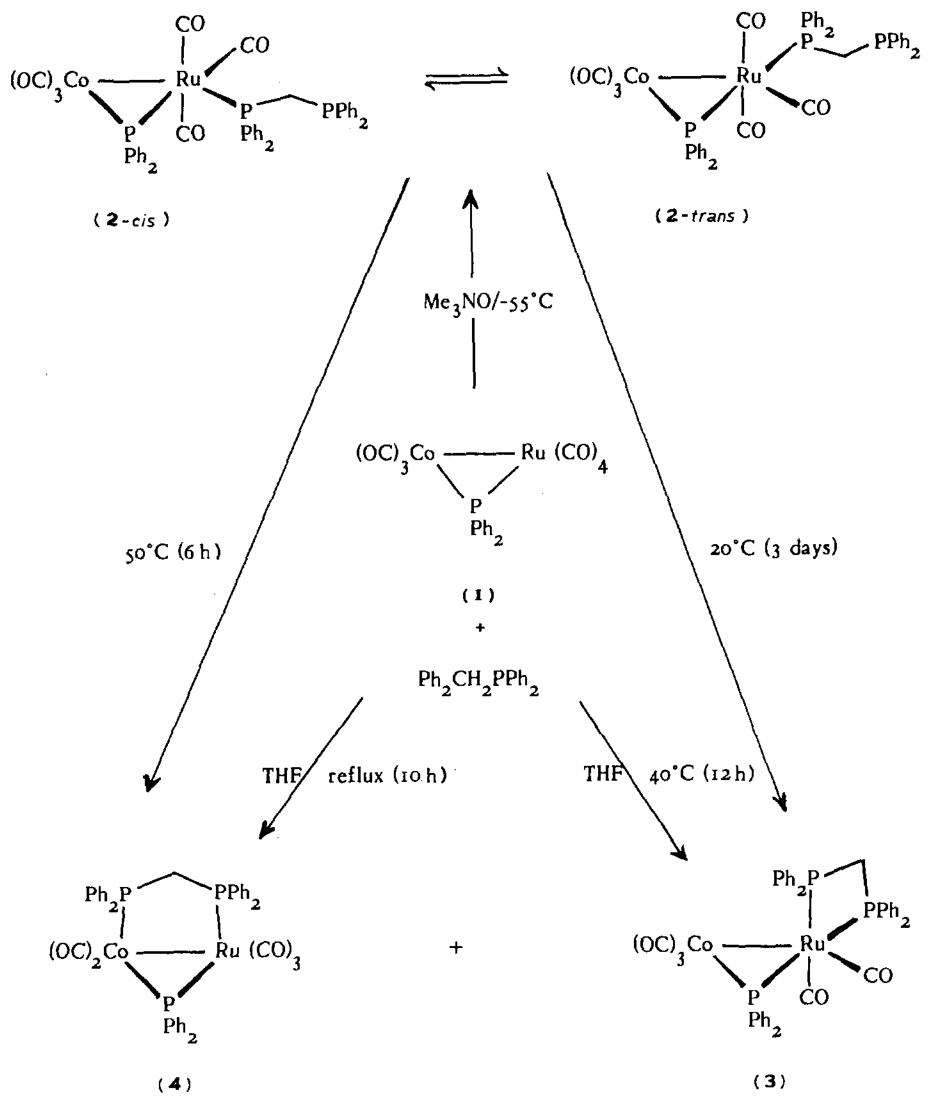
The light-red complex **1** was heated in THF with one equivalent of dppm, under conditions similar to those used for the monosubstitution of a carbonyl of **1** with PPh$_3$ at 50 °C, and the reaction was monitored by thin layer chromatography (TLC) and infrared spectroscopy. The formation of two dark-red products was observed. Appropriate modification of the reaction conditions allowed selective

TABLE 5

MAIN BOND LENGTHS (Å) AND ANGLES (°) IN $(CO)_3Ru(\mu\text{-dppm})(\mu\text{-PPh}_2)Co(CO)_2$ (4)

Ru–Co	2.7580(9)	Ru–P(1)	2.316(2)
Ru–P(2)	2.359(2)	Ru–C(1)	1.888(8)
Ru–C(2)	1.938(8)	Ru–C(3)	1.930(7)
Co–P(1)	2.145(2)	Co–P(3)	2.176(2)
Co–C(4)	1.760(7)	Co–C(5)	1.733(7)
P(1)–C(7)	1.841(7)	P(1)–C(13)	1.818(6)
P(2)–C(6)	1.850(6)	P(2)–C(19)	1.838(6)
P(2)–C(25)	1.819(7)	P(3)–C(6)	1.851(6)
P(3)–C(31)	1.831(6)	P(3)–C(37)	1.821(6)
C(1)–O(1)	1.142(10)	C(2)–O(2)	1.137(10)
C(3)–O(3)	1.142(9)	C(4)–O(4)	1.139(9)
C(5)–O(5)	1.158(9)	P(2)···P(3)	3.018(2)
Co–Ru–P(1)	49.07(4)	Co–Ru–P(2)	95.42(4)
Co–Ru–C(1)	159.2(2)	Co–Ru–C(2)	85.3(2)
Co–Ru–C(3)	82.6(2)	P(1)–Ru–P(2)	144.35(5)
P(1)–Ru–C(1)	110.2(2)	P(1)–Ru–C(2)	87.1(2)
P(1)–Ru–C(3)	85.9(2)	P(2)–Ru–C(1)	105.4(2)
P(2)–Ru–C(2)	86.8(2)	P(2)–Ru–C(3)	93.2(2)
C(1)–Ru–C(2)	96.4(3)	C(1)–Ru–C(3)	95.2(3)
C(2)–Ru–C(3)	167.9(3)		
Ru–Co–P(1)	54.66(4)	Ru–Co–P(3)	90.22(4)
Ru–Co–C(4)	113.9(2)	Ru–Co–C(5)	132.6(2)
P(1)–Co–P(3)	144.41(6)	P(1)–Co–C(4)	101.8(2)
P(1)–Co–C(5)	102.4(2)	P(3)–Co–C(4)	97.6(2)
P(3)–Co–C(5)	97.9(2)	C(4)–Co–C(5)	111.2(3)
Ru–P(1)–Co	76.27(4)	Ru–P(1)–C(7)	118.6(2)
Ru–P(1)–C(13)	118.4(2)	Co–P(1)–C(7)	123.2(2)
Co–P(1)–C(13)	121.5(2)	C(7)–P(1)–C(13)	99.7(3)
Ru–P(2)–C(6)	108.6(2)	Ru–P(2)–C(19)	115.9(2)
Ru–P(2)–C(25)	118.8(2)	C(6)–P(2)–C(19)	103.2(3)
C(6)–P(2)–C(25)	107.2(3)	C(19)–P(2)–C(25)	101.8(3)
Co–P(3)–C(6)	115.4(2)	Co–P(3)–C(31)	112.2(2)
Co–P(3)–C(37)	121.9(2)	C(6)–P(3)–C(31)	102.0(3)
C(6)–P(3)–C(37)	101.9(3)	C(31)–P(3)–C(37)	100.8(3)
Ru–C(1)–O(1)	178.9(3)	Ru–C(2)–O(2)	177.9(3)
Ru–C(3)–O(3)	177.1(3)	Co–C(4)–O(4)	172.9(3)
Co–C(5)–O(5)	174.0(3)	P(2)–C(6)–P(3)	109.3(1)

synthesis of each complex. When complex **1** was heated with one equivalent of dppm in 60 ml of THF at 40 °C for 12 h, IR and TLC monitoring indicated that complex **1** had disappeared and of the two products present, one was largely predominant. Chromatography of the product mixture on a silica-gel column gave 23% of the major complex, which was identified as **3** (Scheme 1). When the same reaction was carried out in refluxing THF for 10 h the starting material **1** disappeared but this time complex **3** was the minor product. Silica-gel column chromatography gave 63% of the major product, which was shown to be **4**. The ^1H NMR spectra of **3** and **4** exhibited only a single triplet for the methylene protons of the dppm ligand. In the $^{31}P\{^1H\}$ NMR spectra of complex **3** at 223 K three signals were observed: a doublet of doublets at low field (δ 187.33 ppm), compatible with a



SCHEME 1

(μ-PPh$_2$)P nucleus coupled with two (dppm) phosphorus nuclei, one *trans* (^2J(P–P) 131.8 Hz) and one *cis* (^2J(P–P) 22.0 Hz) to the phosphido group, and two double doublets at high field (δ −12.47 and −29.02 ppm) (Table 6). These latter signals remain sharp up to ambient temperature, in contrast to the phosphido bridge resonance which broadens markedly as the temperature is raised, owing to the effects of the quadrupole moment of the cobalt nucleus to which it is directly bonded. These results suggest that both phosphorus atoms of the dppm ligand are bonded to the ruthenium atom. The X-ray diffraction study of **3** (vide infra) confirmed that the dppm ligand chelates the ruthenium atom. The ^{31}P{^{1}H} NMR (223 K) spectrum of **4** also showed three doublets of doublets: the resonance at δ 203.5 ppm assigned to the phosphido bridge, along with signals at 47.4 and 24.3

TABLE 6

$^{31}P\{^1H\}$ NMR DATA FOR COMPLEXES **2**-*cis*, **2**-*trans*, **3** and **4** [a]

Complex	μ-PPh_2	Ru-*P*$(Ph)_2CH_2$	Co*P*$(Ph)_2CH_2$	Ph_2PCH_2	$^2J(P_\mu-P_{Ru})$	$^2J(P_\mu-P_{Co})$	$^2J(P_{Ru}-P)$
2-*trans* [b]	184.90(d)	24.30(d)	–	−27.60(d)	104.6(*trans*)	–	115.0
2-*cis* [b]	172.25(s)	29.64(d)	–	−28.40(d)	–	–	104.6
3 [c]	187.33(dd)	−12.47(dd)*trans*	–	–	131.8(*trans*)		43.9
		−29.02(dd)*cis*	–	–	22.0(*cis*)		
4 [c]	203.50(dd)	24.30(dd)	47.40(dd)		92.8	107.4	78.0

[a] In CD_2Cl_2 at 32.38 MHz (δ (ppm); J (Hz)). [b] 193 K. [c] 223 K.

ppm (Table 6). When the temperature of the probe was raised to 305 K only the signal at 24.3 ppm did not broaden; this suggests that the corresponding (dppm) ^{31}P nucleus is bonded to the ruthenium atom while the resonance at 47.4 ppm corresponds to a (dppm) ^{31}P nucleus bonded to cobalt. An X-ray diffraction study of **4** confirmed that the dppm ligand bridges the Ru–Co bond.

The reaction conditions used for the formation of **3** (40 ° C in THF) and **4** (reflux of THF) considered together with the structures of the complexes might suggest that complex **4** is formed from **3** on heating. However, when a pure sample of **3** was heated in THF alone or in the presence of one equivalent of dppm no formation of **4** was observed, and only decomposition of **3** occurred. In view of the facile synthesis of a range of monosubstituted phosphine derivatives of **1** [10] a plausible common intermediate in the formation of **3** and **4** is the monodentate dppm complex **2**. There was no evidence for the formation of **2** at room temperature, and at 40 ° C conversion to **3** would be expected to be rapid. Attempts were then made to prepare a monodentate dppm derivative at low temperatures by use of Me_3NO, a powerful carbonyl displacing reagent. Complex **1** in THF at -55 ° C was treated with dry sublimed Me_3NO in the presence of one equivalent of dppm. Silica-gel TLC monitoring indicated the disappearance of **1** and its replacement by a new red-orange complex. After 12 h at -55 ° C compound **2** was isolated as a precipitate in 66% yield. The $^{31}P\{^1H\}$ (193 K) of **2** showed two signals at low field, a doublet at δ 184.90 ppm and a singlet at δ 172.25 ppm, indicating the presence of two isomers. In the light of our previous studies of phosphine monosubstituted derivatives of **1** [10] these resonances can be seen to be typical of phosphido bridges in two isomeric species having phosphine ligands respectively *trans* or *cis* to the μ-PPh_2 group coordinated to a pseudo-octahedral ruthenium atom. This is confirmed by the ^{31}P signals of the dppm ligands. Thus the **2**-*trans* isomer exhibits a double doublet ^{31}P resonance at δ 24.30 ppm, due to the phosphorus nucleus of the Ph_2PCH_2 group bound to the ruthenium atom and coupled to both the $(\mu\text{-}PPh_2)^{31}P$ and the free $(Ph_2PCH_2)^{31}P$ nuclei (Table 6). The **2**-*cis* isomer shows a doublet at 29.64 ppm for the ^{31}P nucleus of the coordinated Ph_2PCH_2 ligand, coupled only to the uncoordinated phosphorus atom of the dppm. These two isomers undergo exchange on warming, with the intensities of the signals arising from the **2**-*trans* isomer increasing at the expense of the **2**-*cis* species as the temperature increases: ^{31}P NMR (32.38 MHz, CD_2Cl_2): **2**-*trans*/**2**-*cis*: 26/74 (193 K); 29/71 (248 K); 34/66 (273 K). The isolation and characterisation of **2** was followed by attempts to convert these monodentate dppm derivatives into the chelate complex **3** and the bridged compound **4**. IR monitoring of a solution of **2** in THF at ambient temperature revealed a slow conversion into 3 and subsequently the appearance of 4. However, after 3 d at room temperature the relative proportions of products 3 and 4 remained unchanged, indicating that under these conditions 3 is not spontaneously transformed into 4. Fractional crystallisation of the mixture afforded 3 (32%) and 4 (9%). Stirring a solution of 2 in THF at 50 °C for 6 h gave complex 4 as the major product, with 3 present in only minor amounts. Work-up from dichloromethane/hexane gave 4 in 45% yield.

These results suggest that in the displacement of a carbonyl group from 2 by the uncoordinated end of the dppm ligand, the formation of the chelate complex 3 is favoured at ambient temperature. Heating of 2 favours 4 containing a μ-dppm ligand. No evidence was observed for the intramolecular isomerisation of 3 to 4 or vice versa. Instead, on heating 3 appears only to decompose even under CO atmosphere. Although strain within the 4-membered ring of a dppm chelate complex $Ph_2\overline{PMP(Ph)_2C}H_2$ might be expected to facilitate chelate → bridge isomerisation in bi- or polynuclear systems, few examples of such rearrangements have been unequivocally demonstrated [5]. In the specific case of 3 → 4, decoordination of one end of the dppm ligand of 3 must be followed by migration of a CO group from cobalt to ruthenium in order to preserve the overall molecular formula. In the absence of evidence for transformations 3 → 4 and 4 → 3, it thus appears that the formations of 3 and 4 result from competitive intramolecular carbonyl displacement reactions on complex 2, the reaction at the cobalt site being favored on heating at the expense of that at ruthenium site.

Description and discussion of the structures of $(dppm)(OC)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ (3) and of $(OC)_3Ru(\mu\text{-}PPh_2)(\mu\text{-}dppm)Co(CO)_2$ (4)

ORTEP plots of the molecular structures of 3 and 4 are shown in Figs. 1 and 2, respectively. Figure 3 shows the most salient structural features of 3 and 4 together with those of the related complex $(Ph_3P)(OC)_3Ru(\mu\text{-}PPh_2)Co(CO)_3$ (5) [10] for comparison.

In complex 3 the $Ru–PPh_2–Co$ moiety of the precursor 1 is retained, but two carbonyl groups on the pseudo-octahedral ruthenium atom have been replaced by the two phosphorus atoms of a chelating dppm ligand. One phosphorus atom (P(3)) lies approximately *trans* to the phosphido bridge (P(1)–Ru–P(3) 158.92(3)°) while the other (P(2)) occupies an axial site *trans* to the carbonyl ligand C(2)–O(2) (P(2)–Ru–C(2) 163.5(2)°) and *cis* to the phosphido bridge (P(2)–Ru–P(1) 103.57(3)°). Chelation of the dppm ligand results in a severely strained four-membered $\overline{RuPCP}$ ring, with angles at C(6) (P(2)–C(6)–P(3) 97.8(1)°) and Ru (P(2)–Ru–P(3) 70.68(3)°) deviating considerably from the ideal tetrahedral and octahedral angles, respectively. It is interesting that the P(2) atom of the dppm ligand in 3 occupies an axial (*trans* to CO) site other than the equatorial *cis* position, *trans* to the Co–Ru bond. In all previously reported complexes of the type $L_2(CO)_2Ru(\mu\text{-}PPh_2)Co(CO)_3$ [10] (L = tertiary phosphine) the phosphines occupy mutually *cis* equatorial positions. Only for the secondary phosphine Ph_2PH was an axially substituted phosphine obtained. In the case of dppm it is possible that the isomer with two phosphorus atoms equatorial and *trans* to the μ-PPh_2 and Co–Ru bond is disfavoured because of unfavourable steric interactions between the phosphido bridge phenyl groups and a coplanar PPh_2 unit of the chelate. An alternative

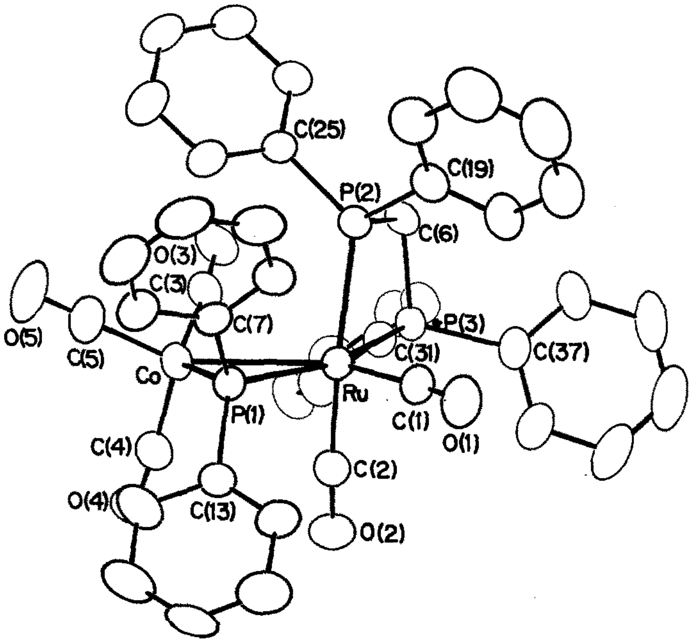


Fig. 1. A perspective view of the molecular structure of (dppm)(CO)$_2$Ru(μ-PPh$_2$)Co(CO)$_3$ (3).

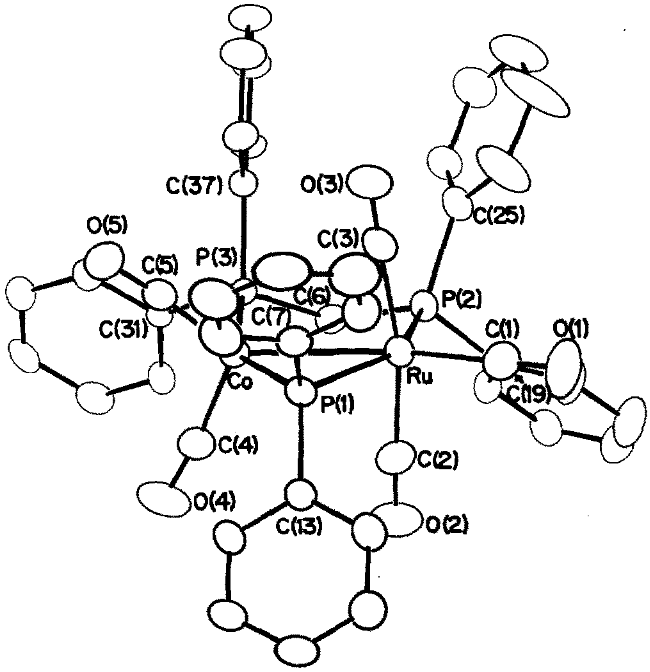
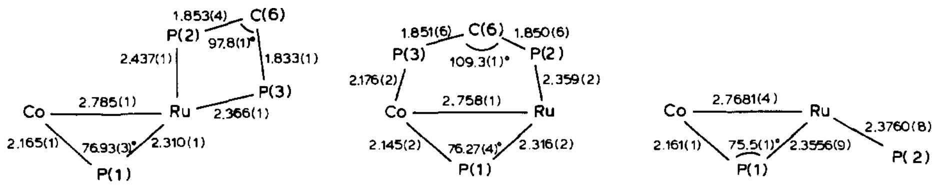


Fig. 2. The molecular structure of (CO)$_3$Ru(μ-PPh$_2$)(μ-dppm)Co(CO)$_2$ (4).



(3) (4) (5)

Fig. 3. Structural data for the Ru(μ-PPh$_2$)Co moiety in complexes **3**, **4** and **5**.

explanation is that axial coordination of one end of the dppm molecule, *trans* to a ligand of high *trans* influence (CO), maximises metal–CO bonding while reducing strain in the Ru–PCP ring by weakening the Ru–P(2) bond. There are, in fact, distinct differences in the Ru–P(3) (2.366(1) Å) and Ru–P(2) (2.437(1) Å) bond lengths, with the latter significantly longer than any of the other Ru–P bond lengths in **3**, **4** or **5** (Fig. 3).

In complex **4** the Ru and Co stereochemistries are remarkably similar to those in **3**, but the dppm ligand now bridges the two metal atoms (Fig. 2). Formally complex **4** results from the exchange of the axial P(2) atom on ruthenium with the equatorial CO group C(3)–O(3) on the cobalt atom of **3**. The large P(1)–Co–P(3) (144.41(6)°) and P(1)–Ru–P(2) (144.35(5)°) angles are consistent with the large ^2J(P(1)–P(2)) (107.4 Hz) and ^2J(P(1)–P(3)) (92.8 Hz) coupling constant values. The Ru–P(2) bond length (2.359(2) Å) is quite similar to the corresponding Ru–P(3) bond length (2.366(1) Å) in **3**. The Co–P(3) bond distance (2.176(2) Å) is comparable to Co–P bond distance (2.173(13) Å) in (Ph$_3$P)(OC)$_3$Ru(μ-PPh$_2$)Co(CO)$_2$PPh$_3$ [12]. As expected, the RuCoPCP five-membered ring is not particularly strained, as shown by the angles P(2)–C(6)–P(3) 109.3(1)°; Co–Ru–P(2) 95.42(4)° and Ru–Co–P(3) 90.22(4)°.

A comparison of structural parameters for the Ru–(μ-P)–Co fragments in **3**, **4** and **5** (Fig. 3) indicates that the phosphido-bridged metal–metal bond is relatively insensitive to phosphine substitution on the metals, although **4** with a dppm bridge has a slightly shorter Ru–Co bond length [Ru–Co 2.785(1) Å in **3**; 2.7681(6) Å in **5** and 2.758(1) Å in **4**]. The angle Ru–P–Co likewise changes little from the chelate (76.93(3)°) to the bridged (76.27(4)°) complex.

Conclusion

Selective routes have been developed to Ru-dppm monodentate (**2**), Ru-dppm chelate (**3**) or Ru-Co-dppm bridged (**4**) derivatives of (OC)$_4$Ru(μ-PPh$_2$)Co(CO)$_3$ (**1**), for which ^{31}P NMR and X-ray diffraction studies established the structural characteristics and demonstrated the retention of the Ru(μ-PPh$_2$)Co moiety. It is shown that (i) the chelate (**3**) and the bridged (**4**) isomers are both formed via the same Ru-dppm monodentate derivative (**2**), (ii) they do not undergo interconversion, (iii) the isomers **3** and **4** are formed by competitive carbonyl displacement reactions, either at the Ru site or at the Co site, by the free end of the dppm ligand of **2**, and (iv) an increase in the temperature favors bridging over chelation of the dppm ligand.

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References

1 See for example: (a) M.J. Breen and G.L. Geoffroy, Organometallics, 1 (1982) 1437; (b) V.D. Patel, A.A. Cherkas, D. Nucciarone, N.J. Taylor and A.J. Carty, Organometallics, 4 (1985) 1792; (c) R.P. Rosen, G.L. Geoffroy, C. Bueno, M.R. Churchill and R.B. Ortega, J. Organomet. Chem., 254 (1983) 89; (d) D.F. Jones, P.H. Dixneuf, A. Benoit and J.Y. Le Marouille, J. Chem. Soc., Chem. Commun., (1982) 1217; (e) R. Regragui, P.H. Dixneuf, N.J. Taylor and A.J. Carty, Organometallics, 3 (1984) 1020; (f) R. Bender, P. Braunstein, P. Metz, and P. Lemoine, Organometallics, 3 (1984) 381; (g) D.A. Young, Inorg. Chem., 20 (1981) 2049; (h) D.G. Evans, G.R. Hughes, D.M.P. Mingos, J.M. Basset and A.J. Welch, J. Chem. Soc., Chem. Commun., (1980) 1255, and references therein.

2 (a) A.D. Harley, G.J. Guskey and G.L. Geoffroy, Organometallics, 2 (1983) 53; (b) R.A. Jones, T.C. Wright, J.L. Atwood and W.E. Hunter, Organometallics, 2 (1983) 470; (c) S.A. MacLaughin, N.J. Taylor and A.J. Carty, Organometallics, 2 (1983) 1194; (d) S.-K. Kang, T.A. Albright, T.C. Wright and R.A. Jones, Organometallics, 4 (1985) 666; (e) J.S. Field, R.J. Haynes, D.N. Smit, K. Natarajan, O. Scheidsteger and O. Huttner, J. Organomet. Chem., 240 (1982) C43; (f) B.F.G. Johnson, J. Lewis, W.J.H. Nelson, J.N. Nicholls and M.D. Vargas, J. Organomet. Chem., 249 (1983) 255.

3 (a) R. Regragui, P.H. Dixneuf, N.J. Taylor and A.J. Carty, Organometallics, 3 (1984) 814; (b) W.F. Smith, N.J. Taylor and A.J. Carty, J. Chem. Soc., Chem. Commun., (1976) 896; (c) K. Yasufuku and H. Yamazaki, J. Organomet. Chem., 35 (1972) 367; (d) R. Zolk and H. Werner, J. Organomet. Chem., 252 (1983) C53; (e) Y.-F. Yu, J. Gallucci and A. Wojcicki, J. Am. Chem. Soc., 105 (1983) 4826 and J. Chem. Soc., Chem. Commun., (1984) 653; (f) S.-G. Shyu and A. Wojcicki, Organometallics, 4 (1985) 1457; (g) S. Rosenberg, G.L. Geoffroy and A.L. Rheingold, Organometallics, 4 (1985) 1184; (h) A.D. Horton, M.J. Mays and P.R. Raithby, J. Chem. Soc., Chem. Commun., (1985) 247.

4 (a) S.A. MacLaughin, J.P. Johnson, N.J. Taylor, A.J. Carty and E. Sappa, Organometallics, 2 (1983) 275; (b) J.C. Jeffery and J.G. Laurence-Smith, J. Chem. Soc., Chem. Commun., (1985) 275; (c) L. Chem, D.J. Kountz and D.W. Meek, Organometallics, 4 (1985) 598; (d) R.E. Ginsburg, R.K. Rothrock, R.G. Finke, J.P. Collman and L.E. Dahl, J. Am. Chem. Soc., 101 (1979) 6550; (e) J.S. McKennis and E.P. Kyba, Organometallics, 2 (1983) 1249; (f) W.C. Mercer, G.L. Geoffroy and A.L. Rheingold, Organometallics, 4 (1985) 1418; (g) S. Rosenberg, R.R. Whittle and G.L. Geoffroy, J. Am. Chem. Soc., 106 (1985) 5934.

5 (a) D.M. McEwan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Chem. Commun., (1982) 1240; (b) P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1983) 889; (c) A.T. Hutton, P.G. Pringle and B.L. Shaw, Organometallics, 2 (1983) 1889; (d) B. Chaudret, S. Sabo and D. Gervais, J. Organomet. Chem., 258 (1983) C19; (e) M.R. Awang, J.C. Jeffrey and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1983) 2091; (f) J.C. Jeffrey, A.G. Orpen, W.T. Robinson, F.G.A. Stone and M.J. Went, J. Chem. Soc., Chem. Commun., (1984) 396; (g) J.A. Iggo, D.P. Markham, B.L. Shaw and M. Pett-Thorton, J. Chem. Soc., Chem. Commun., (1985) 432; (h) B. Delavaux, B. Chaudret, F. Dahan and R. Poilblanc, Organometallics, 4 (1985) 935; (i) B. Chaudret, F. Dahan and S. Sabo, Organometallics, 4 (1985) 1490; (j) B. Delavaux, B. Chaudret, N.J. Taylor, S. Arabi and R. Poilblanc, J. Chem. Soc., Chem. Commun., (1985) 805; (k) A.T. Hutton, G.R. Langrich, D.M. McEvan, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1985) 2121; (l) G.B. Jacobsen, B.L. Shaw and M. Thornton-Pett, J. Chem. Soc., Chem. Commun., (1986) 13; (m) B. Delavaux, B. Chaudret, J. Devillers, F. Dahan, G. Commenges and R. Poilblanc, J. Am. Chem. Soc., 108 (1986) 3703; (n) D.M. McEvan, D.P. Markham, P.G. Pringle and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1986) 1809; (o) S.W. Carr and B.L. Shaw, J. Chem. Soc., Dalton Trans., (1986) 1815; (p) B.D. Alexander, B.J. Johnson, S.M. Johnson, A.L. Casalnuovo and L.H. Pignolet, J. Am. Chem. Soc., 108 (1986) 4405.

6 S. Guesmi, P.H. Dixneuf, N.J. Taylor and A.J. Carty, J. Organomet. Chem., 303 (1986) C47.

7 R. Regragui and P.H. Dixneuf, J. Organomet. Chem., 239 (1982) C12.

8 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, Great Britain, 1974.

9 A.J. Carty, G.N. Mott, N.J. Taylor and J.E. Yule, J. Am. Chem. Soc., 100 (1978) 351.

10 (a) R. Regragui, P.H. Dixneuf, N.J. Taylor and A.J. Carty, Organometallics, 5 (1986) 1; (b) S. Guesmi, P.H. Dixneuf, N.J. Taylor and A.J. Carty, ibid., 5 (1986) 1964.

11 E. Roland and H. Vahrenkamp, Organometallics, 2 (1983) 183.

12 H.C. Foley, W.C. Finch, C.G. Pierpont and G.L. Geoffroy, Organometallics, 1 (1982) 1379.