Synthesis and Crystal Structure of $[Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\overline{PCH{=}CHC}_6H_4)]$,* a Complex with an Unprecedented Phospha-bicyclic Ligand, obtained from $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ *via* Reductive Elimination Reactions

Daniele Belletti, Antonio Tiripicchio, and Marisa Tiripicchio Camellini
Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, I-43100 Parma, Italy
Enrico Sappa
Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via Pietro Giuria 7, I-10125 Torino, Italy

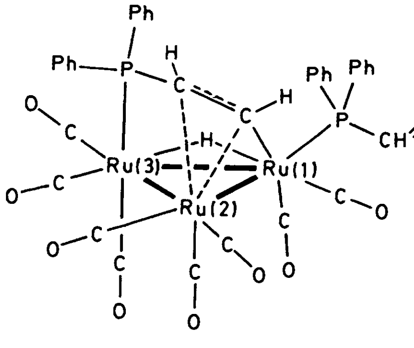
The complex $[Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\overline{PCH{=}CHC}_6H_4)]$ has been obtained by thermal treatment of $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ *via* reductive elimination of ethylene and benzene and metal–metal cleavage. The heterocyclic $\overline{PCH{=}CHC}_6H_4$ bridging ligand, obtained upon activation of co-ordinated diphenyl(vinyl)phosphine, is unprecedented. The complex has been identified by spectroscopic methods and its structure fully elucidated by *X*-ray diffraction methods.

In recent years increasing evidence has been obtained which indicates that μ-phosphido[1] and μ_3-phosphinidene[2] bridges, long considered flexible and inert stabilizing ligands, may easily undergo insertion of alkynes into M–P bonds forming phospha-alkenyl bridges;[3] such reactions are likely to occur also in the homogeneous catalytic hydrogenation of t-butylacetylene[4] and of diphenylacetylene[5] in the presence of phosphido-bridged triruthenium carbonyl clusters.

The chemistry of the phospha-alkenyl ligands is hence of interest in view of their hypothesized intermediacy in catalytic reactions; we have, therefore, started an investigation of new synthetic strategies leading to phospha-alkenyl and allenyl ligands with the aim of gaining better knowledge of their structural features and reactivity patterns.

One of the approaches attempted to the synthesis of complexes with M–P–C–C–M bridging systems was the reaction of $[Ru_3(CO)_{12}]$ with diphenyl(vinyl)phosphine; the final, high-yield derivative was the oxidative-addition product $[Ru_3(\mu\text{-}H)(CO)_8(Ph_2PCH{=}CH_2)(\mu_3\text{-}Ph_2PCH{=}CH)]$ (1),[6] characterized by *X*-ray diffraction methods and multinuclear n.m.r. spectroscopy. This complex seemed to us a potential candidate for the synthesis of new phosphido- or phosphinidene-bridged clusters with co-ordinated hydrocarbyl ligands; indeed, in the light of previous experience, we expected reductive elimination of the cluster hydride† and of the vinyl group of the dangling phosphine to form ethylene and a μ-PPh_2 or, alternatively, the reductive elimination of benzene from a PPh_2 phenyl and the hydride.[7]

During the thermal treatment of complex (1) we have indeed observed the elimination of the cluster hydride and of $CH{=}CH_2$ with formation of a μ-PPh_2 bridge; however, the loss of a ruthenium atom also occurs and, finally, formation of a bridging μ-$\overline{PCH{=}CHC}_6H_4$ phospha-bicyclic ensemble *via* elimination of benzene (presumably from the bridging $Ph_2PCH{=}CH$ ligand). The result of this complex reaction sequence is the P–C bond cleavage of one phosphine molecule, and the activation of another, upon co-ordination to $[Ru_3(CO)_{12}]$ followed by oxidative addition and reductive elimination, to form a phosphorus-containing organic ligand, still bonded to metal atoms. The complex obtained $[Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\overline{PCH{=}CHC}_6H_4)]$ (2) has been identified by spectroscopic methods and its structure fully elucidated by *X*-ray diffraction methods.



(1)

Experimental

Preparation of Complex (2).—Treatment of a bright yellow solution of complex (1) in toluene–octane [5:95 v/v; toluene was necessary for improving the solubility of (1)] under N_2 for 5 min at reflux gave a limpid red-brown solution which, upon evaporation to small volume under reduced pressure, was chromatographed on preparative t.l.c. plates [Kieselgel P. F. Merck; eluant, light petroleum (b.p. range 40—70 °C)–diethyl ether (80:20 v/v)]; seven separate bands were observed and

---

* μ-Benzophosphol-1-yl-μ-diphenylphosphido-bis(tricarbonylruthenium).

† The evidence obtained until now indicates that the presence of cluster-bound hydrides is one of the requisites for these reactions to occur.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex (**2**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru(1)	2 795(1)	1 503(1)	1 387(1)
Ru(2)	4 128(1)	1 562(1)	4 210(1)
P(1)	2 217(3)	1 199(1)	3 730(4)
P(2)	4 525(3)	1 043(1)	2 164(4)
O(1)	4 205(11)	2 041(4)	−998(13)
O(2)	1 467(12)	796(4)	−756(14)
O(3)	1 117(12)	2 380(4)	1 743(14)
O(4)	2 973(10)	2 422(4)	5 755(14)
O(5)	5 270(12)	1 032(4)	6 967(13)
O(6)	6 171(8)	2 262(3)	3 441(11)
C(1)	3 713(13)	1 848(5)	−115(17)
C(2)	1 943(14)	1 079(6)	12(16)
C(3)	1 715(14)	2 049(5)	1 588(16)
C(4)	3 369(13)	2 097(5)	5 200(16)
C(5)	4 838(13)	1 236(5)	5 948(18)
C(6)	5 451(11)	1 988(4)	3 755(14)
C(7)	1 901(10)	550(4)	3 955(13)
C(8)	949(12)	351(5)	3 002(15)
C(9)	672(14)	−146(6)	3 163(18)
C(10)	1 307(13)	−435(5)	4 224(16)
C(11)	2 297(14)	−237(5)	5 153(18)
C(12)	2 564(12)	276(5)	5 032(15)
C(13)	881(11)	1 459(4)	4 559(14)
C(14)	949(13)	1 543(5)	6 141(16)
C(15)	−121(14)	1 733(5)	6 834(18)
C(16)	−1 156(15)	1 805(6)	5 936(19)
C(17)	−1 236(15)	1 707(6)	4 390(21)
C(18)	−170(12)	1 534(5)	3 670(16)
C(19)	4 553(11)	384(4)	2 258(14)
C(20)	5 561(14)	212(5)	1 598(15)
C(21)	5 926(12)	1 066(5)	1 181(12)
C(22)	6 576(12)	1 465(5)	677(15)
C(23)	7 647(14)	1 383(6)	−26(18)
C(24)	8 075(14)	901(7)	−230(18)
C(25)	7 425(14)	496(6)	281(18)
C(26)	6 358(12)	583(5)	989(14)

collected, with some decomposition. The colours of the products were (top to bottom of the plates, with estimated yields in parentheses) yellow (20), yellow (10), purple (10), orange-yellow (25), yellow (5), green-brown (1), and purple (1%).

The first yellow band turned out to be complex (**2**); the fourth product was the unreacted complex (**1**). The second (yellow) and third bands probably correspond to hydrocarbyl-substituted phosphido-bridged clusters; these show indeed only terminal carbonyl stretchings, phenyl signals and complex patterns in the CH and CH_2 region in the ^1H n.m.r. spectra (no hydrides were detected), and signals in the ^{31}P n.m.r. spectra respectively at +155.7 (s), +33.2 (s), and +213.0 (dd), +177.0 (d), and +146.0 (d) p.p.m. The low-yield product bands 5—7 were not investigated.

Complex (**2**) (Found: C, 46.2; H, 2.4; P, 9.1; Ru, 29.2. Calc. for $C_{26}H_{16}O_6P_2Ru_2$: C, 45.25; H, 2.35; P, 9.0; Ru, 29.5%). I.r. (ν_{CO}, in heptane): 2 084ms, 2 072vs, 2 060s, 2 050vs, 2 030vs, 2 010vs, and 1 994vs cm^{-1}. N.m.r. ($CDCl_3$, 25 °C): ^1H, δ 7.86—7.32 (mm) (14 H, PPh, ligand C_6H_4), 7.19—7.16 (d) [*J*(H–H) = 7.7], 7.07—7.04 (d) [*J*(H–H) = 7.7] [1 H, C(20)H*, *J*(P–H) = 31.9], 5.03—5.00 (d) [*J*(H–H) = 7.7], 4.88—4.85 (d) [*J*(H–H) = 7.7] [1 H, C(19)H, *J*(P–H) = 40.0 Hz]; ^{31}P (external 85% H_3PO_4), δ +102.2—101.4 (d) [1 P, *J*(P–P) = 94.6] and +66.7—65.9 (d) p.p.m. [1 P, *J*(P–P) = 93.1 Hz].

Crystal Structure Determination of Complex (**2**).—*Crystal data.* $C_{26}H_{16}O_6P_2Ru_2$, *M* = 688.50, monoclinic, *a* = 11.017(5), *b* = 27.601(8), *c* = 8.834(4) Å, β = 93.49(2)°, *U* = 2 681(2) Å^3 (by least-squares refinement from the θ values of 30 carefully measured reflections), λ = 0.710 69 Å, space group $P2_1/n$, *Z* = 4, D_c = 1.706 g cm^{-3}, *F*(000) = 1 352, μ(Mo-K_α) = 12.59 cm^{-1}. Crystal dimensions 0.18 × 0.23 × 0.27 mm.

Data collection and processing. Siemens AED diffractometer, θ—2θ scan mode, using niobium-filtered Mo-K_α radiation. All the reflections in the range $3 < \theta < 25°$ were measured. Of 5 182 independent reflections, 1 963, having $I > 2\sigma(I)$, were considered observed and used in the analysis. Absorption ignored.

Structure analysis and refinement. Patterson and Fourier methods, full-matrix least-squares refinement with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms except the carbon atoms of the phenyl groups, which were treated isotropically. The hydrogen atoms were placed at their geometrically calculated positions and introduced in the last calculations with fixed isotropic thermal parameters. The weighting scheme used in the last cycles was $w = K[\sigma^2(F_0) + gF_0^2]^{-1}$ with *K* = 0.6742 and *g* = 0.0058. Final *R* and *R'* values 0.0414 and 0.0438. The SHELX system of computer programs was used.[8] Atomic scattering factors, corrected for anomalous dispersion, were taken by ref. 9. All calculations were performed on the Gould POWERNODE 6040 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica' del C.N.R., Parma. Final atom co-ordinates for the non-hydrogen atoms are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

Results and Discussion

Some spectroscopic data for complex (**2**) are worthy of note. The ^{31}P n.m.r. spectrum indicates the presence of two non-equivalent phosphorus atoms coupled each to the other; the signal at +102 p.p.m. could be attributed to the μ-PPh_2 ligand by analogy with the results observed for $[Ru_2(CO)_6(\mu\text{-}PPh_2)_2]$ [+110.9 (s) p.p.m.],[10a] a complex with a structure closely comparable to that of (**2**), as discussed below. In the ^1H n.m.r. spectrum the signals due to the C_6H_4 part of the PCH=CHC_6H_4 ligand fall in the same range as those of μ-PPh_2 and are not attributable; by contrast, the hydrogens on C(19) and C(20) give two doublets of doublets, as expected for two adjacent hydrogens coupled to each other (*J* = 7.7 Hz) and to P(2) (*J* = 40 and 32 Hz respectively). The attribution is based on the smaller *J*(P–H) expected for the hydrogen on C(20).

A perspective view of the structure of complex (**2**) with the atomic numbering scheme is shown in the Figure. Selected bond distances and angles are given in Table 2.

The structure of (**2**) consists of a $Ru_2(CO)_6$ framework, in which the Ru atoms are doubly bridged by phosphorus atoms from a phosphido ligand and from, to our knowledge, a new phospha-bicyclic ligand. By considering the Ru–Ru separation, 2.820(2) Å, as a metal–metal bond, each Ru atom is in a distorted octahedral arrangement. The dihedral angle between the two bridges is 105.1(1)°. The two bridges are nearly symmetrical, with Ru–P bonds comparable in both bridges [range 2.347(4)—2.367(4) Å]. The Ru_2P_2 core in complex (**2**) is very similar to that found in the structure of $[Ru_2(CO)_6(\mu\text{-}PPh_2)_2]$.[10b]

The PCH=CHC_6H_4 ligand is worthy of some attention. It is probably formed by the bridging Ph_2PCH=CH ligand in (**1**) *via* reductive elimination of benzene, from one phenyl and one hydrogen of the remaining phenyl, and subsequent condensation. Even if the whole ligand is perfectly planar [maximum deviation from mean plane 0.01(1) Å], in the penta-atomic ring the double bond character seems to be localized on the C–C

---

* The carbon atoms are labelled as in the Figure.

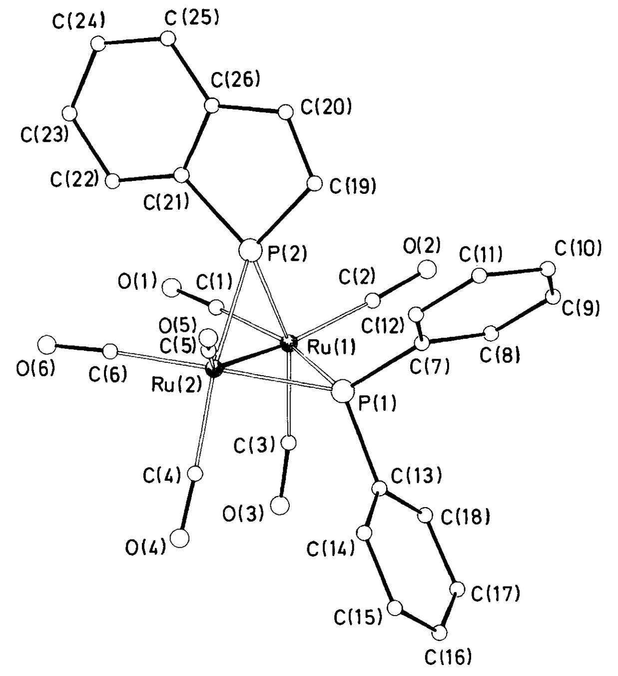


Figure. View of the structure of complex (**2**) showing the atomic numbering scheme

Table 2. Selected bond distances (Å) and angles (°) in complex (**2**)

Ru(1)–Ru(2)	2.820(2)	C(20)–C(26)	1.473(20)
Ru(1)–P(1)	2.356(4)	C(21)–C(26)	1.428(19)
Ru(1)–P(2)	2.357(4)	C(21)–C(22)	1.402(19)
Ru(2)–P(1)	2.347(4)	C(22)–C(23)	1.384(21)
Ru(2)–P(2)	2.367(4)	C(23)–C(24)	1.426(26)
Ru(1)–C(1)	1.965(15)	C(24)–C(25)	1.416(25)
Ru(1)–C(2)	1.893(15)	C(25)–C(26)	1.386(21)
Ru(1)–C(3)	1.936(15)	C(1)–O(1)	1.111(19)
Ru(2)–C(4)	1.933(14)	C(2)–O(2)	1.142(20)
Ru(2)–C(5)	1.906(15)	C(3)–O(3)	1.139(19)
Ru(2)–C(6)	1.935(12)	C(4)–O(4)	1.123(18)
P(2)–C(19)	1.821(12)	C(5)–O(5)	1.142(19)
P(2)–C(21)	1.818(13)	C(6)–O(6)	1.141(15)
C(19)–C(20)	1.370(20)		
Ru(2)–Ru(1)–P(1)	53.0(1)	C(21)–C(22)–C(23)	118.7(13)
Ru(2)–Ru(1)–P(2)	53.5(1)	C(22)–C(23)–C(24)	120.5(14)
Ru(1)–Ru(2)–P(1)	53.3(1)	C(23)–C(24)–C(25)	121.2(15)
Ru(1)–Ru(2)–P(2)	53.2(1)	C(24)–C(25)–C(26)	117.8(15)
Ru(1)–P(1)–Ru(2)	73.7(1)	C(20)–C(26)–C(21)	113.3(12)
C(7)–P(1)–C(13)	100.2(5)	C(20)–C(26)–C(25)	125.8(13)
Ru(1)–P(2)–Ru(2)	73.3(1)	C(21)–C(26)–C(25)	120.9(13)
C(19)–P(2)–C(21)	92.5(6)	Ru(1)–C(1)–O(1)	177.9(13)
P(2)–C(19)–C(20)	109.8(9)	Ru(1)–C(2)–O(2)	174.9(14)
C(19)–C(20)–C(26)	115.6(12)	Ru(1)–C(3)–O(3)	177.1(14)
P(2)–C(21)–C(22)	130.2(10)	Ru(2)–C(4)–O(4)	176.6(13)
P(2)–C(21)–C(26)	108.9(9)	Ru(2)–C(5)–O(5)	178.3(14)
C(22)–C(21)–C(26)	121.0(12)	Ru(2)–C(6)–O(6)	175.2(11)

bond [C(19)–C(20) 1.370(20) and C(20)–C(26) 1.473(20) Å] and the phosphorus atom shows a distorted sp^3 hybridization [angles at phosphorus in the range 73.3(1)—125.0(4)°].

The reaction mechanism leading to the formation of this ligand is of interest, even though no evidence for it is available. The expected reductive elimination of the cluster-bound hydride of complex (**1**) and of the vinyl group of the dangling phosphine occurs, to give an ethylene molecule. This process is unexpectedly accompanied by the loss of a $Ru(CO)_2$ moiety.

The further reductive elimination of benzene to give the phospha-bicyclic ligand, as discussed above, cannot be evidenced, and certainly the presence of side (or intermediate) unidentified products makes it more difficult to make any statement on this point. The drastic reaction conditions adopted were because of the stability of complex (**1**) in solution, even in air. The recovery of about 25% of unreacted (**1**) after thermal treatment also demonstrates this.

Reductive elimination of benzene is apparently a common process in phosphido- and phosphinidene-bridged clusters;[7,8] it has also been found for diphosphines such as $Ph_2PCH_2CH_2PPh_2$, which, in the presence of external hydrogen, gives a μ-$PhPCH_2CH_2PPh_2$ ligand on a triruthenium cluster.[11] Orthometallation reactions of the phenyl groups of co-ordinated PPh_3 were reported by Nyholm.[12] In all these examples, phosphorus-containing metallacyclic rings were formed; by contrast, the formation of (**2**), involving elimination of benzene from a molecule of the phosphine and cocyclization of the remaining substituents, to give an heterocyclic organic ligand, is probably the first example reported of such a reaction in metal carbonyl chemistry.

Further experiments under milder conditions, aimed at trapping reaction intermediates, are in progress.

Acknowledgements

Financial support for this work has been obtained by the Consiglio Nationale delle Richerche, Rome, and by the Italian Ministero della Pubblica Istruzione. Johnson-Matthey is acknowledged for a loan of $RuCl_3$.

References

1 A. J. Carty, S. A. MacLaughlin, and D. Nucciarone, 'Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis; Organic Compounds and Metal Complexes,' eds. J. . Verkade and D. L. Quinn, Verlag Chemie, New York, 1987, ch. 16, p. 559.
2 G. Huttner and K. Knoll, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 743.
3 K. Knoll, G. Huttner, and L. Zsolnai, *J. Organomet. Chem.*, 1986, **312**, C 57; 1987, **332**, 175; K. Knoll, G. Huttner, T. Fässler, and L. Zsolnai, *ibid.*, 1987, **327**, 255; K. Knoll, H. Huttner, and K. Evertz, *ibid.*, **333**, 97; K. Knoll, G. Huttner, L. Zsolnai, and O. Orama, *Angew Chem.*, 1986, **98**, 1099; *J. Organomet. Chem.*, 1987, **337**, 379; J. Lunniss, S. A. MacLaughlin, N. J. Taylor, A. J. Carty, and E. Sappa, *Organometallics*, 1985, **4**, 2066.
4 M. Castiglioni, R. Giordano, and E. Sappa, *J. Organomet. Chem.*, 1988, **342**, 111; 1989, **362**, 399.
5 M. Castiglioni, R. Giordano, and E. Sappa, *J. Organomet. Chem.*, 1989, **369**, 419.
6 R. Gobetto, E. Sappa, A. Tiripicchio, M. Tiripicchio Camellini, and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, in the press.
7 M. Lanfranchi, A. Tiripicchio, E. Sappa, and A. J. Carty, *J. Chem. Soc.*, Dalton Trans., 1987, 2737 and refs. therein; F. Van Gastel, S. A. MacLaughlin, M. Lynch, A. J. Carty, E. Sappa, A. Tiripicchio, and M. Tiripicchio Camellini, *J. Organomet. Chem.*, 1987, **326**, C 65 and refs. therein; M. A. Pellinghelli, A. Tiripicchio, E. Sappa, A. J. Carty, and F. Van Gastel, IV European Symposium on Inorganic Chemistry, Freiburg, Abstracts, p. A 6.
8 G. M. Sheldrick, SHELX Program for crystal structure determination, University of Cambridge, 1976.
9 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
10 (*a*) R. P. Rosen, G. L. Geoffroy, C. Bueno, M. R. Churchill, and R. B. Ortega, *J. Organomet. Chem.*, 1983, **254**, 89; (*b*) A. J. Carty, personal communication.
11 M. I. Bruce, M. L. Williams, J. M. Patrick, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1986, 2557.
12 C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 1972, 87; C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 1973, 529.

Received 25*th April* 1989; *Paper* 9/01721F