Organometallics 1991, 10, 3282–3286

X-ray Structural Analysis of 10. Single crystals were grown from hexane at −15 °C. Crystal data collection parameters are summarized in Table II. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied; the minimal transmission was 81%. The structure was solved by direct methods (SHELXS-86). Atomic coordinates (see Table III) and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares. The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by the riding method. For other details see Table II.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support, the Fonds in particular for a Doktorandenstipendium for U. Wecker and M. Schulz. We also gratefully acknowledge support by Dr. G. Lange and F. Dadrich (mass spectra), Dr. C. Burschka (X-ray analysis), T. Daniel and D. Schneider (NMR spectra), U. Neumann, R. Schedl, and C. P. Kneis (elemental analyses), and DEGUSSA AG (chemicals).

Supplementary Material Available: Drawing of complex 10 showing the atom numbering scheme and tables of bond distances, bond angles, least-squares planes, positional parameters, and general displacement parameter expressions (11 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Cluster Chemistry. 69.[1] Unusual Transformation of Triarylphosphine Ligands on a Pentanuclear Ruthenium Cluster. X-ray Structures of Two Phases of $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$

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The reaction between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ and PPh_3 gave a monosubstituted complex, which in refluxing CH_2Cl_2 was transformed into $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4, Ar = Ph). This complex contains a distorted-octahedral PRu_5 cluster with the PPh_2 groups bridging basal Ru–Ru edges, together with a C_2Ph_2 ligand spanning an Ru_3 face. A similar reaction with $P(tol)_3$ (tol = $C_6H_4Me\text{-}p$) gave $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ar)(\mu\text{-}PPh_2)(\mu\text{-}PAr_2)(CO)_{10}$ (4, Ar = tol). The net reaction occurring on the Ru_5 cluster is between PAr_3 (Ar = Ph, tol) and C_2PPh_2 to form PPh, PAr_2, and PhC_2Ar ligands. The molecular structure of 4 (Ar = Ph) was determined from X-ray studies on solvent-free and solvated modifications. $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$: triclinic, space group $P\bar{1}$, $a = 17.282\ (4)$ Å, $b = 13.558\ (2)$ Å, $c = 13.498\ (4)$ Å, $\alpha = 61.94\ (1)°$, $\beta = 81.06\ (2)°$, $\gamma = 85.03\ (2)°$, $Z = 2$, $R = 0.037$, $R' = 0.036$ for 6084 observed reflections. $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}\cdot CH_2Cl_2$: triclinic, space group $P\bar{1}$, $a = 21.399\ (10)$ Å, $b = 12.658\ (15)$ Å, $c = 12.447\ (8)$ Å, $\alpha = 59.00\ (7)°$, $\beta = 79.20\ (4)°$, $\gamma = 74.22\ (8)°$, $Z = 2$, $R = 0.067$, $R' = 0.085$ for 5442 observed reflections.

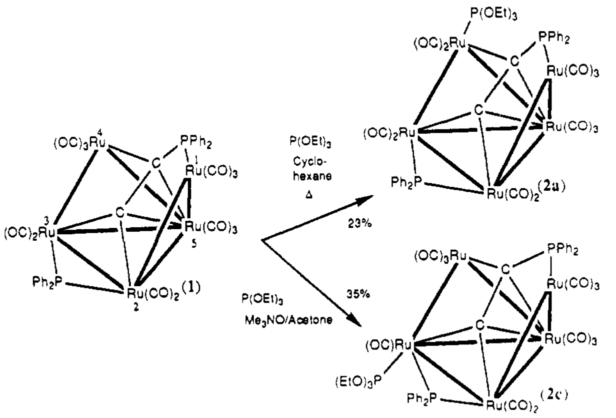
Introduction

We have recently shown that the preferred sites of CO substitution by tertiary phosphines or phosphites in $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1; Scheme I) are at Ru(3) (thermally induced reactions) or at Ru(4) (in Me_3NO-facilitated reactions) to give isomers of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PR_3)$ (2a, 2c).[1] In studies with $P(OEt)_3$, no subsequent modification of the group 15 ligand occurred; the product obtained with PMe_2Ph was noted as being unstable, but the decomposition products were not characterised. We have now found that facile rearrangement reactions of triarylphosphines occur with 1; these are described below.

Results and Discussion

Two methods of substituting CO ligands in 1 by PPh_3 were examined. The first method, using Me_3NO to remove a CO ligand, permitted the isolation of dark brown crystalline $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)$ (3, Ar = Ph). In the FAB mass spectrum, a molecular ion was found at

Scheme I. Reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) with $P(OEt)_3$



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[1] Part 68: Bruce, M. I.; Liddell, M. J.; Nicholson, B. K.; Skelton, B. W.; Tiekink, E. R. T.; White, A. H. *J. Organomet. Chem.*, in press.

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Scheme II. Reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1) with PAr_3 (Ar = Ph, tol)

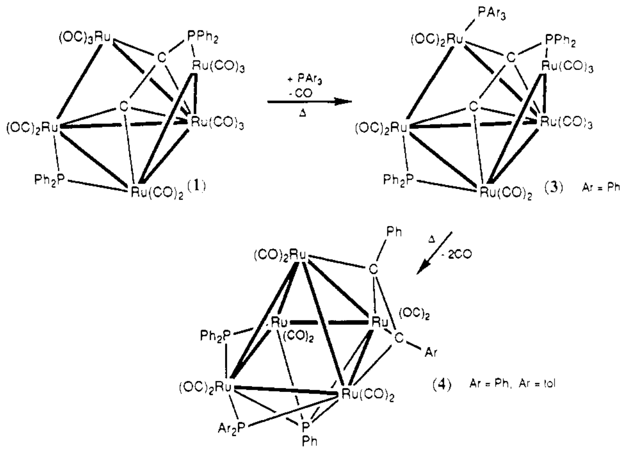

Table I. Significant Bond Distances (Å) and Angles (deg) in $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4, Ar = Ph)

	Distances		
Ru(1)-Ru(2)	2.781 (1)	Ru(3)-P(2)	2.358 (3)
Ru(1)-Ru(4)	2.911 (1)	Ru(3)-P(3)	2.250 (2)
Ru(1)-Ru(5)	2.840 (1)	Ru(4)-P(1)	2.365 (3)
Ru(2)-Ru(3)	2.845 (1)	Ru(4)-P(2)	2.482 (2)
Ru(2)-Ru(5)	2.734 (1)	Ru(4)-P(3)	2.391 (3)
Ru(3)-Ru(4)	2.851 (1)	Ru(1)-C(1)	2.315 (6)
Ru(3)-Ru(5)	2.812 (1)	Ru(2)-C(1)	2.094 (7)
Ru(4)-Ru(5)	2.9015 (9)	Ru(2)-C(2)	2.227 (6)
Ru(1)-P(1)	2.298 (2)	Ru(5)-C(2)	1.991 (6)
Ru(1)-P(2)	2.392 (2)	C(1)-C(2)	1.39 (1)
Ru(2)-P(2)	2.322 (2)		
	Angles		
Ru(1)-C(1)-Ru(2)	78.0 (2)	C(1)-C(2)-Ru(5)	107.4 (4)
Ru(2)-C(2)-Ru(5)	79.5 (2)	C(1)-C(2)-C(201)	123.1 (6)
		C(2)-C(1)-C(101)	124.1 (5)

m/z 1499, which fragmented by loss of 12 CO groups. The ν(CO) region of the IR spectrum was similar to that of **2a** in both the appearance and position of the bands. The ^{31}P NMR spectrum confirmed that the cluster was monosubstituted, and from the IR data, it seems likely that the substitution occurred at Ru(4) (Scheme II).

The second method involved heating a mixture of 1 and PPh_3 in refluxing CH_2Cl_2 for 20 h. From this reaction mixture, complex 3 (Ar = Ph) and dark green crystalline $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4, Ar = Ph) were isolated, the latter as a hexane solvate. A similar complex, $Ru_5(\mu_4\text{-}PPh)\{\mu_3\text{-}\eta^2\text{-}PhC_2(tol)\}(\mu\text{-}PPh_2)\{\mu\text{-}P(tol)_2\}(CO)_{10}$ (4, Ar = tol), was isolated from the direct thermal reaction of $P(tol)_3$ with 1 in CH_2Cl_2. Complex 3 (Ar = Ph) was converted into 4 (Ar = Ph) by heating in CH_2Cl_2, demonstrating the intermediacy of 3 in the synthesis of 4. The FAB mass spectra of 4 (Ar = Ph, tol) showed molecular ions at *m/z* 1444 and 1485, respectively, each of which fragmented by loss of 10 carbonyl groups. These data indicated that the complexes were related to 1 by addition of PR_3 and loss of three carbonyl groups.

Molecular Structure of $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$. The molecular structure of 4 (Ar = Ph) was determined by X-ray studies of crystals from both hexane and dichloromethane, these being obtained as two distinct phases; crystals of the latter were inferior, being solvated and twinned. The molecules in both crystals are similar, and plots of a molecule present in the unsolvated crystals are shown in Figures 1 and 2. Significant bond distances and angles are collected in Table I. Values cited below are drawn from the more precise study of the unsolvated complex.

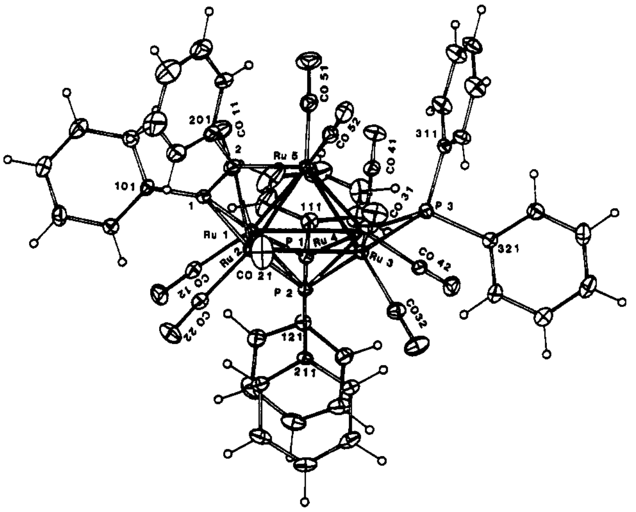

Figure 1. Single molecule of the unsolvated form of $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4). 20% thermal ellipsoids are shown for the non-hydrogen atoms, with labeling. Hydrogen atoms have arbitrary radii of 0.1 Å.

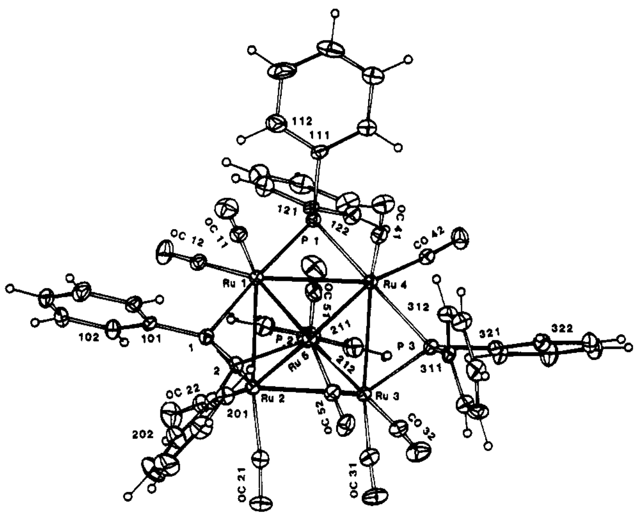

Figure 2. View of the unsolvated form of $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4) down the P(2)-Ru(5) axis of the cluster.

The complex is a derivative of the well-known cluster $Ru_5(\mu_4\text{-}PPh)(CO)_{15}$ (5), which has a square-pyramidal Ru_5 metal skeleton, of which the square base is capped by the μ_4-phenylphosphinidene group;[2] the PRu_5 core has distorted-octahedral geometry. In 4 (Ar = Ph), two carbonyls are found on each of the ruthenium atoms. Two adjacent basal edges are bridged by diphenylphosphido groups, one of which is derived from the triphenylphosphine. Relative to the basal Ru_4 plane, P(1) lies below and P(3) above; the former is adjacent to the μ_3-alkyne ligand and takes up the sterically least congested position. A $\mu_3,\eta^2\text{-}PhC_2Ph$ ligand bridges the Ru(1)Ru(2)Ru(5) face.

The Ru-Ru bond distances (2.734 (1)-2.911 (1) Å) are within the usual values, the shortest distance being Ru(1)-Ru(5). The Ru-P distances of the phosphido and phosphinidene ligands are in the range 2.250 (2)-2.482 (2) Å. The phosphinidene is coordinated in a similar fashion to that found in 5, with three normal Ru-P bonds ($Ru\text{-}P_{av}$ 2.36 Å) and one long bond Ru(4)-P(2) (2.482 (2) Å).

Comparison with the parent complex $Ru_5(\mu_4\text{-}PPh)(CO)_{15}$ (5)[2] enables the structural effects of the various bridging

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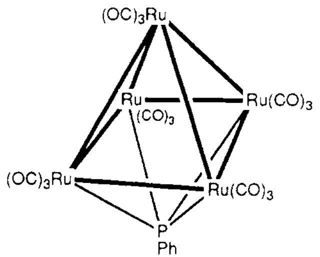
[2] Natarajan, K.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1981**, *209*, 85.

Table II. Non-Hydrogen Atom Coordinates in $Ru_5(\mu_4\text{-}PPh)(\mu^3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4, Ar = Ph)

atom	*x*	*y*	*z*
Ru(1)	0.74056 (3)	0.33394 (4)	0.05496 (4)
Ru(2)	0.86034 (3)	0.33546 (3)	−0.10920 (5)
Ru(3)	0.81377 (3)	0.12405 (5)	−0.07412 (5)
Ru(4)	0.68793 (3)	0.11975 (4)	0.09163 (4)
Ru(5)	0.71039 (3)	0.30914 (5)	−0.13298 (5)
C(11)	0.6495 (4)	0.4290 (6)	0.0255 (6)
O(11)	0.5960 (3)	0.4878 (5)	0.0072 (5)
C(12)	0.7923 (4)	0.4001 (6)	0.1221 (6)
O(12)	0.8232 (4)	0.4368 (5)	0.1656 (5)
C(21)	0.9254 (5)	0.3273 (6)	−0.2289 (7)
O(21)	0.9661 (4)	0.3315 (6)	−0.3064 (6)
C(22)	0.9503 (4)	0.3795 (6)	−0.0761 (6)
O(22)	1.0058 (3)	0.4043 (5)	−0.0574 (6)
C(31)	0.8457 (4)	0.1487 (6)	−0.2241 (6)
O(31)	0.8666 (3)	0.1571 (5)	−0.3114 (4)
C(32)	0.8843 (4)	0.0018 (6)	−0.0291 (6)
O(32)	0.9290 (3)	−0.0689 (5)	−0.0082 (5)
C(41)	0.5815 (4)	0.1642 (6)	0.0795 (6)
O(41)	0.5167 (3)	0.1906 (5)	0.0794 (4)
C(42)	0.6713 (4)	−0.0264 (5)	0.2153 (6)
O(42)	0.6651 (3)	−0.1103 (4)	0.2904 (4)
C(51)	0.6052 (4)	0.3619 (6)	−0.1494 (6)
O(51)	0.5445 (3)	0.4014 (5)	−0.1703 (5)
C(52)	0.7171 (4)	0.3070 (6)	−0.2698 (6)
O(52)	0.7200 (3)	0.3093 (4)	−0.3564 (4)
P(1)	0.6827 (1)	0.1929 (1)	0.2208 (1)
C(111)	0.5849 (4)	0.2100 (6)	0.2861 (6)
C(112)	0.5624 (6)	0.3074 (7)	0.2894 (7)
C(113)	0.4879 (6)	0.3166 (8)	0.3441 (9)
C(114)	0.4386 (5)	0.2289 (8)	0.3920 (7)
C(115)	0.4606 (5)	0.1319 (8)	0.3918 (8)
C(116)	0.5345 (5)	0.1235 (7)	0.3389 (7)
C(121)	0.7347 (4)	0.1266 (6)	0.3453 (5)
C(122)	0.7528 (5)	0.0151 (6)	0.4006 (6)
C(123)	0.7899 (5)	−0.0294 (7)	0.4968 (7)
C(125)	0.7918 (5)	0.1515 (8)	0.4835 (7)
C(126)	0.7531 (5)	0.1942 (6)	0.3895 (6)
P(2)	0.8244 (1)	0.1809 (1)	0.0636 (1)
C(211)	0.9995 (4)	0.1091 (5)	0.1719 (5)
C(212)	0.9026 (4)	−0.0054 (6)	0.2150 (6)
C(213)	0.9524 (5)	−0.0572 (6)	0.2950 (7)
C(214)	0.9875 (5)	0.0003 (7)	0.3349 (7)
C(215)	0.9737 (5)	0.1120 (7)	0.2941 (7)
C(216)	0.9253 (4)	0.1664 (6)	0.2124 (6)
P(3)	0.6993 (1)	0.0365 (2)	−0.0318 (2)
C(311)	0.6358 (4)	0.0722 (5)	−0.1399 (6)
C(312)	0.5614 (4)	0.1121 (7)	−0.1334 (6)
C(313)	0.5151 (5)	0.1385 (7)	−0.2188 (7)
C(314)	0.5446 (5)	0.1256 (7)	−0.3116 (7)
C(315)	0.6194 (5)	0.0849 (7)	−0.3194 (6)
C(316)	0.6646 (4)	0.0575 (6)	−0.2348 (6)
C(321)	0.6958 (4)	−0.1151 (6)	0.0372 (6)
C(322)	0.6408 (4)	−0.1724 (6)	0.0198 (6)
C(323)	0.6385 (5)	−0.2956 (6)	0.0734 (7)
C(324)	0.6906 (5)	−0.3484 (6)	0.1482 (7)
C(325)	0.7468 (5)	−0.2952 (7)	0.1678 (8)
C(326)	0.7489 (5)	−0.1795 (6)	0.1127 (7)
C(1)	0.7878 (4)	0.4721 (5)	−0.1228 (6)
C(101)	0.7952 (4)	0.5860 (5)	−0.1349 (5)
C(102)	0.8559 (4)	0.6151 (6)	−0.0980 (6)
C(103)	0.8596 (5)	0.7226 (6)	−0.1134 (7)
C(104)	0.8035 (5)	0.8006 (6)	−0.1630 (7)
C(105)	0.7436 (5)	0.7735 (6)	−0.1995 (7)
C(106)	0.7384 (4)	0.6659 (6)	−0.1851 (6)
C(2)	0.7695 (4)	0.4512 (5)	−0.2077 (5)
C(201)	0.7831 (4)	0.5343 (6)	−0.3315 (6)
C(202)	0.8540 (5)	0.5870 (7)	−0.3783 (7)
C(203)	0.8667 (6)	0.6646 (8)	−0.4908 (8)
C(204)	0.8084 (6)	0.6923 (8)	−0.5566 (7)
C(205)	0.7369 (6)	0.6453 (7)	−0.5120 (7)
C(206)	0.7239 (4)	0.5647 (6)	−0.3993 (6)

groups to be gauged. The average basal Ru–Ru separations are 2.847 and 2.864 Å in 4 and 5, respectively; the average basal–apical distances are 2.822 and 2.840 Å, respectively. Both show a shortening of ca. 0.02 Å in the substituted complex. The equatorial Ru–Ru bonds bridged by the μ-PPh_2 groups are 2.851 and 2.911 Å, while that bridged by C(1) of the alkyne is shortened to 2.781 Å. The basal–apical Ru–Ru bond bridged by C(2) is also the shortest at 2.734 Å, while that spanned by the C_2 unit is longer at 2.840 Å. Compared with 5, the Ru_3 face capped by the alkyne is significantly contracted in size.



(5)

The average Ru–PPh bond lengths are 2.388 and 2.375 Å in 4 and 5, respectively; the apical Ru atoms are 1.976 and 1.99 Å above the basal plane, and the phosphinidene P atoms are 1.285 and 1.235 Å below this plane.

The μ-PPh_2 groups form asymmetric bridges, with P(1)–Ru distances of 2.298 (2) and 2.365 (3) Å and P(3)–Ru distances of 2.250 (2) and 2.391 (3) Å. The location of these groups above and below the Ru_4 plane may be related to the alternating behavior of the $Ru(CO)_3$ groups in 5, where adjacent Ru atoms have two CO groups above and below the basal plane. In both complexes, the origins of this feature are probably electronic in nature.

The alkyne is coordinated to the Ru_3 face by two long Ru–C bonds (Ru(1)–C(1) 2.315 (6), Ru(2)–C(2) 2.227 (6) Å) and two short bonds (Ru(5)–C(2) 1.991 (6), Ru(2)–C(1) 2.094 (7) Å), a pattern suggesting a bonding mode intermediate between μ_3,η^2-$\|$ and μ_3,η^2-$\perp$. This is possibly due to a solid-state freezing out of the oscillatory motion that has been noted for other μ_3,η^2-$\|$ complexes in solution.[3] The C≡C bond length of 1.39 (1) Å is similar to that found in other μ_3,η^2-acetylene complexes.[4]

In terms of electron counting, complex 4 is electron precise. The five Ru atoms gain the required 50e from eight Ru–Ru bonds (16e), ten CO ligands (20e), the PPh group (4e), two PPh_2 groups (6e), and the alkyne (4e), although individually Ru(4) is electron rich while Ru(5) is electron poor.

The spectroscopic properties of complexes 4 in solution are in accord with the solid-state structure. The ^1H NMR spectrum of 4 (Ar = tol) indicated that there were two types of Me group in the ratio 2/1; these were assigned to the tolyl groups on the μ-$P(tol)_2$ and $PhC_2(tol)$ ligands, respectively. The ^{31}P NMR spectrum of 4 (Ar = Ph) showed that the two μ-PPh_2 groups were nearly equivalent, a broad signal being found at δ 203.7. In contrast, there were two phosphido environments in 4 (Ar = tol); these appeared as separate broad signals at δ 208.7 and 203.7 in acetone but in CH_2Cl_2 as an apparent triplet formed by two overlapping doublets (δ 205.2, 202.4; J_{PP} = 340 Hz). By comparison with 4 (Ar = Ph), it seems likely that the high-field signal was due to the μ-PPh_2 group and the low-field signal to the μ-$P(tol)_2$ ligand. The μ_4-PPh groups in 4 (Ar = Ph, tol) gave signals at δ 451.5 and 451.4, respectively.

From the above results, it is evident that the reaction of 1 with PPh_3 under mild conditions has resulted in initial

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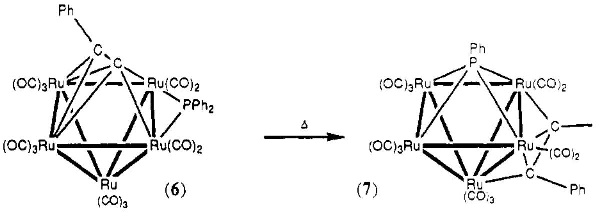
[3] Aime, S.; Bertoncello, R.; Busetti, V.; Gobetto, R.; Granozzi, G.; Osella, D. *Inorg. Chem.* **1986**, *25*, 4004.

[4] Gastel, F. V.; MacLaughlin, S. A.; Lynch, M.; Carty, A. J.; Sappa, E.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1987**, *326*, C65.

Scheme III. Phenyl Migration in $Ru_5(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{14}$



substitution of CO to give **3** (Ar = Ph). The use of Me_3NO enabled the isolation of **3** (Ar = Ph) in 65 min in yields (46%) comparable to those obtained in 20 h by the thermal route. This reactivity may be contrasted with that of $P(OEt)_3$ where, for a given reaction time, the Me_3NO and thermal routes gave similar yields.[1] However, in the case of $P(OEt)_3$, the isomer distribution in the two reactions differed, whereas with PPh_3 only one isomer of **3** (Ar = Ph) was obtained. These results are in accord with recent studies on CO substitution in $Ru_3(CO)_{12}$ showing that reactions of $P(OEt)_3$ occur at slightly lower rates than PPh_3 under Me_3NO activation[5] but at considerably higher rates under thermal activation.[6]

The difference in product distribution between $P(OEt)_3$ and PPh_3 may be rationalized on steric grounds. Molecular modeling showed that if the PPh_3 were to substitute at Ru(3) (the site of thermal substitution by $P(OEt)_3$) then significant interactions between the phenyl groups of the PPh_3 and $\mu\text{-}PPh_2$ ligands would exist.

The thermal stability of **3** is evidently very low, since on heating facile P–C bond cleavage in the phosphido, phosphinoacetylide, and phosphine ligands occurred. Migration of the aryl groups to the C_2 unit has generated a disubstituted alkyne, and the phosphorus groups have been converted into phosphido and phosphinidene ligands (see Scheme II). This is a new pattern of reactivity for **1**. The precise mode of formation of **4** has not been determined, but several of the rearrangements that might reasonably be invoked have precedents. Thus, initial cleavage of the $C_2\text{–}PPh_2$ bond in **1** to C_2 and PPh_2 fragments (as found in the formation of $Ru_4(\mu_4\text{-}C_2)(\mu\text{-}PPh_2)_2(CO)_{12}$)[7] could be followed by migration of a Ph group from PPh_2 to the C_2 ligand to give C_2Ph and PPh ligands (as found in the thermolysis of $Ru_5(\mu_4\text{-}C_2Ph)(\mu\text{-}PPh_2)(CO)_{14}$ (**6**), which gave $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(CO)_{13}$ (**7**) (Scheme III)[8]). The formation of **4** (Ar = Ph) is somewhat different from the latter reaction in that two aryl groups have migrated to the C_2 unit, one of these originating from the tertiary phosphine rather than from a phosphido group. An alternative single-step route would be the elimination of C_2Ph and formation of PPh from the C_2PPh_2 ligand. It is likely that closure of the Ru_5 skeleton occurs at the stage of generation of the PPh group, which caps the base of the resulting square pyramid.

The remaining reaction to consider is the transfer of an aryl group from the PAr_3 ligand. There are many examples recorded of P–C(aryl) bond cleavage to form PAr_2 groups.[9] The aryl group may be bonded to the cluster as μ-Ar, cyclometalated, dehydrogenated to μ-aryne, or transferred to another cluster-bound ligand. We believe that this is the first occasion that transfer to an acetylide ligand has been observed. An alternative route, transfer of Ar to phenylacetylide and formation of PAr_2 via the intermediacy of a phenylethynylphosphonium ligand, cannot be ruled out.

Although P–C cleavage reactions of PPh_3 generating phosphido groups are well-known,[9] the reaction conditions have generally been quite severe (refluxing toluene, xylene, decalin). The reaction of $Ru_3(\mu\text{-dppm})(CO)_{10}$ with K-Selectride ($K[HBBu^s{}_3]$) resulted in the formation of the dephenylated anion $[Ru_3\{\mu_3\text{-}PPhCH_2PPh_2\}(CO)_9]^-$ at room temperature.[10] In the present case, loss of the aryl group from the coordinated tertiary phosphine has occurred under thermal conditions, which were less forcing than those used by Knox et al.[11] in their synthesis of the benzyne complex $Ru_5(\mu_5\text{-}\eta^6\text{-}C_6H_4)(\mu_4\text{-}PPh)(CO)_{13}$ from $Ru_3(CO)_{11}(PPh_3)$ in refluxing toluene, and indicates considerable activation of PPh_3 by coordination to **1**. The formation of **4** (Ar = Ph) from **3** (Ar = Ph) by multiple CO loss under conditions not affecting **1** indicates that the triarylphosphine substitution of the latter has rendered the cluster more susceptible to CO dissociation. This may be a steric effect, since kinetic studies with $Ir_4(CO)_{12}$ have indicated that arylphosphines induce greater labilization of CO than the smaller ligands such as alkylphosphines or CO.[12]

Conclusions

Triarylphosphine ligands attached to the open Ru_5 cluster present in **1** or **3** are activated toward further reaction and rearrangement under mild conditions. The net reaction is

$$PAr_3 + C_2PPh_2 \rightarrow ArC_2Ph + PAr_2 + PPh$$

which is accompanied by cluster condensation (formation of an extra Ru–Ru bond) and loss of three CO groups.

Experimental Section

General Conditions. All reactions were carried out under dry, high-purity nitrogen with use of standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were performed by the Canadian Microanalytical Service, New Westminster, B.C., Canada V3M 1S3. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Reagents. Complex **1** was prepared by the literature method.[13] Phosphines were from Strem Chemicals, Newburyport, and were used directly. $Me_3NO\cdot 2H_2O$ (Aldrich) was dehydrated by sublimation (100 °C (0.1 mm)).

Instrumentation. A Perkin-Elmer 683 double beam with NaCl optics was used for IR; a Bruker CXP300 was used for ^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz, and ^{31}P NMR at 121.49 MHz; ^{31}P chemical shifts are relative to external 85% H_3PO_4. Spectra recorded in nondeuterated solvents used an external concentric tube containing D_2O for field lock. VG ZAB 2HF was used for FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Syntheses of $Ru_5(\mu_5\text{-}\eta^2,P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)$ (3) and $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ (4, Ar = Ph). (a) Me_3NO-Assisted Reaction. To a solution of **1** (100

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mg, 0.079 mmol) and PPh_3 (21 mg, 0.080 mmol) in acetone (45 mL) was added Me_3NO (6 mg, 0.080 mmol). After 1 h a further portion of Me_3NO (6 mg, 0.080 mmol) was added, and 5 min later complete reaction was indicated by spot TLC. The solvent was removed under vacuum and the residue chromatographed (column, silica). Elution with petroleum spirit/CH_2Cl_2 (7/3) gave a trace orange band followed by a major brown band, which was crystallized (CH_2Cl_2/petroleum spirit) as black crystalline $Ru_5(\mu_5\text{-}\eta^2,P\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{12}(PPh_3)$ (**3**): 55 mg, 0.037 mmol, 46%; mp 184–186 °C; IR (cyclohexane) $\nu(CO)$ 2062 (s), 2028 (s), 2008 (m), 2001 (sh), 1993 (m), 1974 (w), 1968 (sh), 1952 (m) cm^{-1}; ^1H NMR (C_6H_6) δ 7.9–6.6 (m, Ph); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 281.3 (s, PPh_2), 59.8 (s, PPh_3), 41.0 (s, C_2PPh_2). FAB MS, 1499, $[M + H]^+$ (ions formed by loss of 12 CO groups). Two other minor bands were eluted but not characterized, and a large amount of material was also left on the column. Anal. Calcd for $C_{56}H_{35}O_{12}P_3Ru_5$: C, 44.89; H, 2.35; M_r 1498. Found: C, 44.45; H, 2.57; M_r 1498 (mass spectrometry, 1499, $[M + H]^+$).

(b) Thermal Reactions. (i) In CH_2Cl_2. A solution of **1** (100 mg, 0.079 mmol) and PPh_3 (21 mg, 0.080 mmol) was heated in refluxing CH_2Cl_2 (20 mL) for 20 h. After the mixture was cooled and solvent removed under reduced pressure, the residue was purified by TLC (petroleum spirit/CH_2Cl_2, 3/2); a major brown band (R_f 0.44) was separated from seven other bands, and further TLC (petroleum spirit/CH_2Cl_2/acetone, 16/2/1) resolved this product into two bands. A brown band (R_f 0.36) was found to be **3** (54 mg, 0.036 mmol, 45%) (identified by IR, FAB MS), and the remaining green band (R_f 0.43) crystallized (CH_2Cl_2/hexane) to give dark green-black crystals of $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}\cdot 0.5C_6H_{14}$ (**4**, Ar = Ph): 25 mg, 0.017 mmol, 22%; mp 238–240 °C; IR (cyclohexane) $\nu(CO)$ 2044 (vw), 2025 (s), 2013 (sh), 1996 (vs), 1976 (vw), 1970 (vw), 1947 (vw) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7–6.9 (m, 35 H, Ph), 1.42 (m, 4 H, hexane), 0.88 (m, 3 H, hexane); $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 451.5 (s, PPh), 203.7 (m, PPh_2); FAB MS, 1444, $[M + 2 H]^+$ (ions formed by loss of 10 CO groups). Anal. Calcd for $C_{54}H_{35}O_{10}P_3Ru_5\cdot 0.5C_6H_{14}$: C, 46.09; H, 2.85; M_r 1442 (unsolvated). Found: C, 46.15; H, 2.94; M_r 1442 (mass spectrometry, 1444, $[M + 2 H]^+$).

(ii) Conversion of 3 to 4 (Ar = Ph) in CH_2Cl_2. Complex **3** (15 mg, 0.01 mmol) was heated in CH_2Cl_2 (25 mL) at reflux point for 20 h. The solvent was then removed and the residue purified by TLC (petroleum spirit/CH_2Cl_2/acetone, 16/2/1) to give four bands, of which a green band (R_f 0.32) was identified (FAB MS, IR) as **4** (Ar = Ph) (2 mg, 0.007 mmol, 14%) and a brown band (R_f 0.29) as unreacted **3** (12 mg, 80%).

(iii) In 1,2-Dichloroethane. Heating a solution of **1** (50 mg, 0.040 mmol) and PPh_3 (11 mg, 0.042 mmol) in 1,2-dichloroethane (20 mL) for 20 h (oil bath, 106 °C) gave an orange-brown solution. The solvent was removed and the residue separated by TLC (petroleum spirit/CH_2Cl_2/acetone, 16/2/1), giving a complicated array of products (11 bands), of which only a green band (R_f 0.30) (7 mg, 0.005 mmol, 12%) was characterized as **4** (Ar = Ph) (IR, FAB MS).

Synthesis of $Ru_5(\mu_4\text{-}PPh)\{\mu_3\text{-}\eta^2\text{-}PhC_2(tol)\}(\mu\text{-}PPh_2)\{\mu\text{-}P(tol)_2\}(CO)_{10}$ (4, Ar = tol). A reaction between **1** (90 mg, 0.071 mmol) and $P(tol)_3$ (22 mg, 0.71 mmol) in refluxing CH_2Cl_2 (20 mL) for 6 days gave a brown-green solution. The solvent was removed and the residue purified by TLC (petroleum spirit/CH_2Cl_2/acetone, 16/2/1); a major green band was collected and precipitated from CH_2Cl_2/petroleum spirit to give the green solid $Ru_5(\mu_4\text{-}PPh)\{\mu_3\text{-}\eta^2\text{-}PhC_2(tol)\}(\mu\text{-}PPh_2)\{\mu_2\text{-}P(tol)_2\}(CO)_{10}\cdot 0.5C_6H_{14}$ (**4**, Ar = tol): 39 mg, 0.026 mmol, 37%; mp 250 °C dec; IR (cyclohexane) $\nu(CO)$ 2045 (vw), 2025 (s), 2013 (sh), 1997 (vs), 1980 (vw), 1972 (vw), 1949 (vw) cm^{-1}; ^1H NMR (C_6D_6) δ 7.8–6.6 (m, 32 H, Ph + C_6H_4), 1.87 (s, 6 H, Me), 1.85 (m, 3 H, Me), 1.30 (m, 4 H, C_6H_{14}), 0.88 (m, 3 H, C_6H_{14}); $^{31}P\{^1H\}$ (CH_2Cl_2) δ 451.4 (s, PPh), 203.8 (m, PPh_2 + $P(tolyl)_2$); $^{31}P\{^1H\}$ NMR (acetone) δ 452.3 (s, PPh), 208.7 (m, $P(tolyl)_2$), 203.7 (m, PPh_2); FAB MS; 1485, $[M + H]^+$ (ions formed by loss of 10 CO groups). Anal. Calcd for $C_{57}H_{41}O_{10}P_3Ru_5\cdot 0.5C_6H_{14}$: C, 47.19; H, 3.17; M_r (unsolvated) 1484. Found: C, 47.11; H, 3.11; M_r 1484 (mass spectrometry, 1485, $[M + H]^+$).

Crystallography

Unique diffractometer data sets were measured on crystals of both the unsolvated and solvated forms of **4** (Ar = Ph). Crystals of the latter were inferior, and the specimen used was twinned so that, to the best of our ability, a single-reciprocal lattice was measured and processed; nonetheless, the precision of the determination is inevitably inferior to that of the unsolvated form. N independent reflections were measured within the $2\theta_{max}$ given (monochromatic Mo Kα radiation, λ = 0.71073 Å); N_o with $I > 3\sigma(I)$ were considered observed and were used in the 9 × 9 block-diagonal least-squares refinement after Gaussian absorption correction and solution of the structures by direct methods.

Thermal parameters of the non-hydrogen atoms were refined anisotropically (exception: C(22,52,322) of the dichloromethane solvate were ill-behaved and the isotropic form was used); $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R and R' on $|F|$ are quoted at convergence; statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used. Neutral-atom complex scattering factors were employed;[14] computation used the XTAL 2.4 system[15] implemented by S. R. Hall. No extinction effects were observed; the temperature of the determinations was ca. 295 K. Pertinent results are given in the figure and the tables; a common numbering scheme is used, and only the molecule of the unsolvated species depicted as the other, at least in respect of the molecular core, is essentially identical. Supplementary material is comprised of structure factor amplitudes, thermal and hydrogen parameters, and ligand geometries for both forms, together with non-hydrogen atom coordinates for the CH_2Cl_2 solvate.

Crystal and Refinement Data. $Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}$ ($C_{54}H_{35}O_{10}P_3Ru_5$): M_r = 1442.1; triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 17.282 (4), b = 13.558 (2) Å, c = 13.498 (4) Å, α = 61.94 (1)°, β = 81.06 (2)°, γ = 85.03 (2)°, V = 2757 Å^3; $D_c(Z = 2)$ = 1.74 g cm^{-3}; $F(000)$ = 1408; μ_{Mo} = 13.3 cm^{-1}; specimen, 0.06 × 0.14 × 0.23 mm; $A^*_{min,max}$ = 1.07, 1.17; $2\theta_{max}$ = 50°; N = 9623, N_o = 6084; R = 0.037, R' = 0.036; n_v = 650; data range, h, 0 to +20, k, −15 to +16, l, −14 to +15.

$Ru_5(\mu_4\text{-}PPh)(\mu_3\text{-}PhC_2Ph)(\mu\text{-}PPh_2)_2(CO)_{10}\cdot CH_2Cl_2$ ($C_{54}H_{35}O_{10}P_3Ru_5\cdot CH_2Cl_2$): M_r = 1527.1; triclinic, space group $P\bar{1}$, a = 21.399 (10) Å, b = 12.658 (15) Å, c = 12.447 (8) Å, α = 59.00 (7)°, β = 79.20 (4)°, γ = 74.22 (8)°, V = 2776 Å^3; $D_c(Z = 2)$ = 1.83 g cm^{-1}; $F(000)$ = 1492; μ_{Mo} = 14.2 cm^{-1}; specimen, 0.03 × 0.26 × 0.36 mm; $A^*_{min,max}$ = 1.04, 1.38; $2\theta_{max}$ = 45°; N = 7232, N_0 = 5442; R = 0.067, R' = 0.085; n_v = 663; data range, h, 0 to +22, k, −12 to +13, l, −10 to +12.

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Supplementary Material Available: Listings of non-hydrogen thermal parameters, positional parameters, and interatomic distances and angles (16 pages); listings of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

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