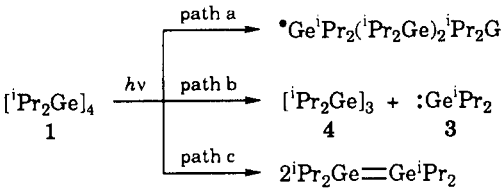
Scheme I



germylene 3, respectively, on the basis of trapping experiments and from a comparison of their spectral characteristics with those of such species previously reported.[10,12,14] No change in absorbance was observed over a 77–143 K temperature range.

Along with laser flash photolysis and matrix isolation experiments, product studies were carried out by photolyzing 1 (0.04 M) with a 110-W low-pressure Hg arc lamp at room temperature for 1 h under argon in cyclohexane. Together with high-boiling unidentified products containing germanium, octaisopropyltetragermane, $(H^iPr_2Ge^iPr_2Ge)_2$ (13%), hexaisopropyltrigermane, $(H^iPr_2Ge)_2Ge^iPr_2$ (2%), and tetraisopropyldigermane, $(H^iPr_2Ge)_2$ (4%), were carefully identified in the photolysate by means of GC–MS and NMR methods. The dihydrotetragermane is likely to arise from the cyclotetragermane 1, which undergoes ring opening to form the intermediate tetragermyl diradical. The tetragermyl diradical in turn abstracts hydrogen from hydrogen sources such as the solvent used in this study and the isopropyl group on the germanium atom. The dihydrotrigermane is explained by the intermediacy of the trigermyl diradical. The trigermyl diradical, which forms from ring opening of the cyclotrigermane $[^iPr_2Ge]_3$ (4) or from the tetragermyl diradical by α-elimination of a germylene, abstracts hydrogen. No formation of a germylene by α-elimination of polygermyl radical has been reported.[14] The dihydrodigermane seems to arise from the intermediacy of the digermene 2 abstracting hydrogen. In order to obtain more information on possible reactive intermediates, cyclohexane solutions of 1 containing carbon tetrachloride were similarly irradiated. Diisopropyldichlorogermane (50%) and 1,2-dichlorotetraisopropyldigermane (45%) were obtained as the main products. The formation of dichlorogermane and dichlorodigermane seems to indicate the intermediacy of the germylene 3 and digermene 2.[16,17] This may be further substantiated by the presence of 1,1-diisopropyl-3,4-dimethyl-1-germacyclopent-3-ene (3%) and 1,1,2,2-tetraisopropyl-4,5-dimethyl-1,2-digermacyclohex-4-ene (1%) for the photolysis of 1 in cyclohexane containing a large amount of 2,3-dimethylbutadiene.[17,18] Photochemically generated germylene species are not trapped effectively by 2,3-dimethylbutadiene.[10,12,14] In the presence of ethanol and 2,2-dimethylpropanol, photolysis of 1 in cyclohexane afforded 1,1,2,2-tetraisopropylethoxydigermane (4%) and 1,1,2,2-tetraisopropyl-*tert*-butoxydigermane (3%), respectively. It is well-known that digermene species can be trapped efficiently by alcohol.[17] On the other hand, photochemically generated germylene species do not react with alcohol.[10,12,14]

These results are best rationalized by three paths described in Scheme I: (a) ring opening of 1 to form the tetragermyl diradical, (b) ring contraction of 1 to give cyclotrigermane 4 with extrusion of germylene 3, and (c) conversion to digermene 2. A route to digermene with sucessive α-elimination of germylene has been proposed in the photodecomposition of octaethylcyclotetragermane.[9] These laser photolysis studies show another route to digermene in the photolysis of octaisopropylcyclotetragermane.

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[19] All new compounds were characterized by ^1H NMR and GC–MS methods.

Cationic and Neutral 50-Electron Triruthenium Carbonyl Clusters Containing Three Bridging Diphenylphosphido Ligands

Javier A. Cabeza*
Departamento de Química Organometálica, Universidad de Oviedo, 33071 Oviedo, Spain
Fernando J. Lahoz and Alberto Martín
Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón,
Facultad de Ciencias, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

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Summary: The reaction of $RuCl_3{\cdot}nH_2O$ with CO in refluxing 2-methoxyethanol and subsequent treatment of the obtained solution with PPh_2H (Ru:P = 1:1), zinc, and CO gives the cationic 50-electron triruthenium complex $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]Cl$ (**1**) in 32% yield. Complex **1** undergoes CO elimination upon UV irradiation to give quantitatively the neutral derivative $[Ru_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_3(CO)_7]$ (**2**). Compounds **1** and **2** react with refluxing propan-2-ol to give the 48-electron hydrido complex $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7]$ (**3**). The molecular structure of complex **2** is reported.

Significant chemistry of diphenylphosphido-bridged organometallics has been developed over the past decade.[1-7] For ruthenium, many trinuclear carbonyl deriv-

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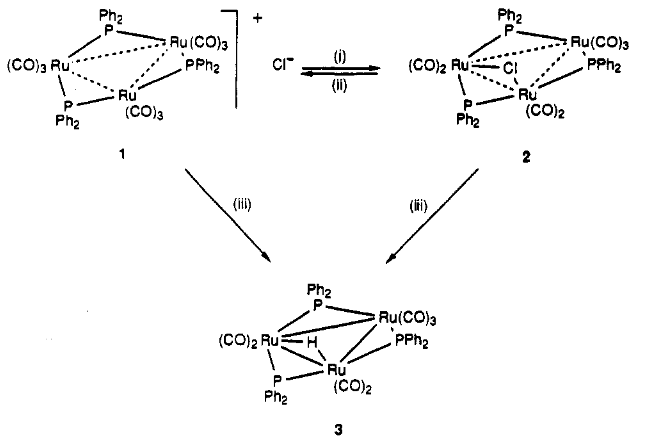
Scheme I[a]



[a] Reagents: (i) $h\nu$; (ii) CO; (iii) refluxing propan-2-ol.

atives are now known, including the complexes $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_n]$ (n = 9, 10),[3d] $[Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8]$,[1c,2,3e] $[Ru_3(\mu\text{-}H)_3(\mu\text{-}PPh_2)_3(CO)_7]$,[1c,2] and $[Ru_3\{\mu_3\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)(CO)_8]$,[5a] which are active hydrogenation catalyst precursors.[4,5a] With the exception of the 46-electron $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9]$[3d] and the 50-electron $[Ru_3\{\mu\text{-}PPh(C_5H_4N)\}(\mu\text{-}PPh_2)(CO)_9]$[5a] and $[Ru_3(\mu_3\text{-}C_2R)(\mu\text{-}PPh_2)(CO)_9]$,[5b] all the other trinuclear diphenylphosphido-bridged ruthenium clusters are 48-electron species. It is also interesting to note that cationic phosphido-bridged compounds are rare[6,7b] and, as far as we are aware, the complexes $[M_2(\mu\text{-}PPh_2)(CO)_8]BF_4$ (M = Fe, Ru) are the only ones which have been described.[6]

We have recently reported a high-yield synthesis of pyrazolate-bridged ruthenium carbonyl complexes starting from $RuCl_3\cdot nH_2O$, CO, pyrazole, and zinc.[8] We now report that this synthetic route leads not only to the first cationic trinuclear ruthenium cluster containing μ-phosphido ligands, namely the 50-electron compound $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]Cl$ (**1**), but also to $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$, a compound which is now attracting considerable attention.[1,2,9] We also describe some reactivity of complex **1** and the X-ray structure of its derivative $[Ru_3(\mu\text{-}Cl)(\mu\text{-}PPh_2)_3(CO)_7]$ (**2**).

The reaction of $RuCl_3\cdot nH_2O$ with CO (1 atm) in refluxing 2-methoxyethanol gives a yellow solution which is a useful precursor for the synthesis of mononuclear ruthenium(II) carbonyl compounds[10] and for the low-pressure preparation of $[Ru_3(CO)_{12}]$.[11] Treatment of this solution with PPh_2H (Ru:P = 1:1) and an excess of granular zinc at reflux temperature, under CO (1 atm), for 3 h gave a yellow solid suspended in a deep red solution. The solid was filtered, recrystallized from CH_2Cl_2–hexane, and characterized[12] as the cationic 50-electron complex $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]Cl$ (**1**; 32% yield, based on Ru). Column chromatography (silica gel) of the solution afforded the known compounds $[Ru_2(\mu\text{-}PPh_2)_2(CO)_6]$[2] (36%) and $[Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7]$[1c,2] (16%) and some other unidentified products.

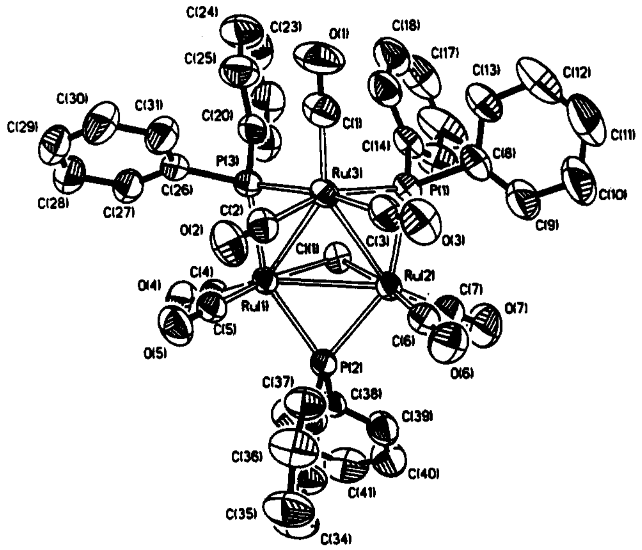


Figure 1. Ortep view of **2**. Selected bond distances (Å) and angles (deg) are as follows: Ru(1)–Ru(2) = 2.9293 (8); Ru(1)–Ru(3) = 3.2222 (7); Ru(2)–Ru(3) = 3.1288 (8); Ru(1)–Cl(1) = 2.453 (2); Ru(2)–Cl(1) = 2.450 (1); Ru(1)–P(2) = 2.361 (2); Ru(1)–P(3) = 2.349 (2); Ru(2)–P(1) = 2.358 (2); Ru(2)–P(2) = 2.363 (2); Ru(3)–P(1) = 2.389 (2); Ru(3)–P(3) = 2.407 (1); Ru(1)–Cl(1)–Ru(2) = 73.4 (1); Ru(2)–P(1)–Ru(3) = 82.5 (1); Ru(1)–P(2)–Ru(2) = 76.7 (1); Ru(1)–P(3)–Ru(3) = 85.3 (1).

The ionic nature of complex **1** was established by measuring its conductivity in acetone.[12] The presence of the chloride ion was confirmed by making the salt $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]BF_4$ via methathesis of complex **1** with $AgBF_4$.[13] The ^{31}P NMR spectrum of **1** showed an AX_2 spin system, at 54.6 and 78.5 ppm, indicating C_s symmetry for the complex. Most 50-electron trinuclear clusters have an open (nonbonded) edge;[5,14] however, the proximity and the low frequencies of the ^{31}P NMR resonances of complex **1** suggest[15] that its three Ru–Ru edges are not very different and that the bonding between the Ru atoms should be of the three-center–four-electron type, therefore having Ru–Ru distances longer than those of 48-electron μ-PPh_2 clusters, which present ^{31}P resonances above 150 ppm.[1–7,16]

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(12) **1**: ν_{CO} (CH_2Cl_2) 2111 (vw), 2086 (w), 2050 (vs), 2020 (w), 1988 (m), 1951 (w) cm^{-1}; ^1H NMR (acetone-d_6, 300 MHz, 298 K, internal $SiMe_4$) δ 7.3–8.2 (m, C_6H_5) ppm; $^{31}P\{^1H\}$ NMR (acetone-d_6, 121.5 MHz, 298 K, external 85% H_3PO_4) δ 78.5 (d, J = 77.4 Hz, 2 P), 54.6 (t, J = 77.4 Hz, 1 P) ppm; Λ_M (1.2×10^{-4} M acetone solution) 126 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd (found) for $C_{45}H_{30}ClO_9P_3Ru_3$: C, 47.15 (47.41); H, 2.64 (2.90).

(13) $[Ru_3(\mu\text{-}PPh_2)_3(CO)_9]BF_4$: the IR and NMR spectra are comparable to those of complex **1**; Λ_M (5.2×10^{-4} M acetone solution) 112 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd (found) for $C_{45}H_{30}BF_4O_9P_3Ru_3$: C, 45.13 (45.02); H, 2.52 (2.71).

(14) See, for example: Arif, A. M.; Bright, T. A.; Jones, R. A.; Nunn, C. M. *J. Am. Chem. Soc.* **1988**, *110*, 6894.

(15) It has been suggested[5b] that the chemical shift of a bridging phosphido ligand is related to the M–P–M angle: the wider the angle the lower the frequency of the ^{31}P resonance. However, exceptions to this rule have also been reported.[5a]

A general theoretical description of these types of electron-rich clusters has been reported.[17]

Some reactivity of **1** is shown in Scheme I. When **1** was irradiated with UV light, in toluene at 10 °C, the neutral 50-electron compound $[Ru_3(\mu\text{-Cl})(\mu\text{-PPh}_2)_3(CO)_7]$ (**2**) was formed quantitatively.[18] Complex **1** was re-formed when a solution of **2** was exposed to carbon monoxide. Complex **2** is soluble in all organic solvents and behaves as a nonelectrolyte in acetone. Its ^{31}P NMR spectrum is rather surprising, since it shows an ABX spin system[18] instead of the expected A_2X spin system, indicating that the complex has C_1 symmetry. The high ^{31}P chemical shifts of this complex (if compared to those of complex **1**) may be rationalized in terms of shorter Ru–Ru distances as a result of the substitution of a chloride for two CO ligands. To confirm this asymmetric structure, a single-crystal X-ray diffraction study was carried out.[19]

The molecular structure of complex **2** is shown in Figure 1. The cluster consists of a triangle of ruthenium atoms with the Ru(1)–Ru(3) and Ru(2)–Ru(3) edges bridged by PPh_2 ligands and the Ru(1)–Ru(2) edge doubly bridged by a chloride and a PPh_2 ligand. Seven CO ligands complete the coordination shell of the metal atoms: three are attached to Ru(3), two to Ru(2), and the remaining two to Ru(1). This ligand distribution gives rise to electronic environments for Ru(1) and Ru(2) different from that of Ru(3). This is evidenced by the fact that the Cl(1) and P(2) bridges are symmetric (i.e. Ru(1)–Cl(1) = 2.453 (2), Ru(2)–Cl(1) = 2.450 (1) Å), whereas the P(1) and P(3) bridges are asymmetric (i.e. Ru(2)–P(1) = 2.358 (2), Ru(3)–P(1) = 2.389 (2) Å). Also, the carbonyl ligands C(2)-O(2) and C(3)O(3), which are attached to Ru(3), present longer Ru–C distances (1.951 (8) and 1.943 (6) Å, respectively) than the other CO ligands (average 1.861 Å), and their carbon atoms are relatively close to Ru(1) and Ru(2) (Ru(1)···C(2) = 3.546 (5), Ru(2)···C(3) = 3.501 (7) Å), suggesting an incipient semibridging situation (Ru(3)–C–O angles 172.6 (5) and 173.7 (6)°, respectively). Curiously, the three intermetallic distances are different: Ru(1)–Ru(2) = 2.9293 (8), Ru(1)–Ru(3) = 3.2222 (7), and Ru(2)–Ru(3) = 3.1288 (8) Å. This asymmetry should be due to local ligand and bridging ligand effects and should not be related to packing effects because it persists in solution, as indicated by ^{31}P NMR spectroscopy (vide supra). The three Ru–Ru distances in **2** are longer than those found in 48-electron clusters,[1-3] probably as a consequence of being a 50-electron cluster. However, unlike other 50-electron clusters (which have an open edge[5,14]), all the intermetallic distances in **2** are short enough to be considered as bonding interactions, although the influence of the bridging ligands in these distances should not be neglected; in fact, the shortest Ru–Ru distance corresponds to the doubly bridged Ru–Ru edge. These data suggest a three-center–four electron bonding type, but theoretical calculations are needed to fully define the situation.

Both **1** and **2** gave the known[1c,2] 48-electron hydride $[Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7]$ (**3**) upon reaction with refluxing propan-2-ol for 3 h (Scheme I). Alcohols at high temperatures have been shown to be good reagents to substitute hydrido ligands for coordinated chlorides.[20] The preparation of **3** from **1** and **2** suggested that **2** might be an intermediate in the transformation of **1** into **3**. In fact, we subsequently proved that complex **1** gives **2** when stirred in refluxing THF for 3 h.

These results indicate that the chloride ligand of complex **2** can be substituted by anionic ligands to give new products which will probably show interesting chemical and catalytic properties, and they complement work on synthetic routes to substituted and activated triruthenium clusters.[21]

Acknowledgment. We thank the DGICYT (Spain) for financial support and a reviewer for helpful comments.

Supplementary Material Available: Details of the structure determination of complex **2**, including listings of crystal and experimental data and solution and refinement details, atomic positional and thermal parameters, H atom coordinates, bond distances and angles, torsion angles, and interatomic contacts (16 pages). Ordering information is given on any current masthead page.

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(18) **2**: ν_{CO} (hexane) 2068 (s), 2027 (vs), 2023 (s, sh), 1988 (m), 1966 (m), 1937 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, 298 K, internal $SiMe_4$) δ 8.4–6.6 (m, C_6H_5) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz, 298 K, external 85% H_3PO_4) ABX spin system (the precise δ of the atoms A and B and the couplings J_{AB}, J_{AX}, and J_{BX} could not be determined since the outer lines of the second-order AB and X parts of the spectrum were not observed: $^1/_2\,(\delta_A + \delta_B) = 148.5$ ppm, δ_X 113.0 ppm, $|J_{AX} + J_{BX}| = 303.1$ Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz, 298 K, internal $SiMe_4$) 199.5 (d, J = 6.1 Hz, 1 CO), 198.1 (d, J = 9.6 Hz, 1 CO), 197.9 (d, J = 9.8 Hz, 1 CO), 197.0 (s, 2 CO), 194.5 (d, J = 12.5 Hz, 1 CO), 193.7 (d, 12.3 Hz, 1 CO), 145–115 (m, C_6H_5) ppm. Anal. Calcd (found) for $C_{43}H_{30}ClO_7P_3Ru_3$: C, 47.36 (47.18); H, 2.77 (2.56).

(19) (a) Crystals of $\mathbf{2}\cdot{}^1/_2Et_2O$ were obtained by slow difussion of hexane layered on a solution of **2** in diethyl ether at −20 °C. Crystal data: $C_{43}H_{30}ClO_7P_3Ru_3\cdot{}^1/_2Et_2O$, $M_r = 1127.35$, triclinic, space group $P\bar{1}$, a = 13.081 (1) Å, b = 13.786 (1) Å, c = 14.705 (1) Å, α = 88.91 (1)°, β = 70.85 (1)°, γ = 68.31 (1)°, V = 2311.9 (4) Å^3, Z = 2, ρ_{calcd} = 1.620 g cm^{-3}, $\lambda(MoK\alpha)$ = 0.71069 Å, $\mu(Mo\ K\alpha)$ = 11.57 cm^{-1}, crystal dimensions 0.56 × 0.23 × 0.20 mm. Cell constants were obtained by least-squares refinement of 56 reflections in the range $20 \le 2\theta \le 32°$. A total of 7146 reflections were measured ($\omega/2\theta$ scan technique) at room temperature on a Siemens-Stoe AED-2 diffractometer in the range $3 \le 2\theta \le 47°$; 5146 observed reflections ($F \ge 5.0\sigma(F)$) were used in the refinement. An empirical absorption correction was applied.[19b] The structure was solved by Patterson methods and refined anisotropically with the SHELX76 system on a MICROVAX 3400 computer. A disordered Et_2O molecule was included in the later cycles of refinement. Hydrogen atoms were included in calculated positions, refined with a riding model. Final R and R_w values were 0.033 and 0.037; weights were in the form $w = 0.735(\sigma^2(F) + 0.00146F^2)^{-1}$. (b) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* 1983, *39*, 158.

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