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PHOTOINDUCED FORMATION OF PHOSPHIDO-BRIDGED CLUSTERS DERIVED FROM $Ru_3(CO)_9(PPh_2H)_3$. CRYSTAL AND MOLECULAR STRUCTURE OF $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$

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Summary

The new complex $Ru_3(CO)_9(PPh_2H)_3$ (I) was prepared by the direct thermal reaction of $Ru_3(CO)_{12}$ with PPh_2H and was spectroscopically characterized. Irradiation of I with $\lambda \geq 300$ nm leads to the formation of $Ru_2(\mu\text{-}PPh_2)_2(CO)_6$ (II) and three new phosphido-bridged complexes, $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8$ (III), $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_7(PPh_2H)$ (IV) and $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ (V). These complexes have been characterized spectroscopically and $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ by a complete single crystal X-ray structure determination. It crystallizes in the space group $P2_1/n$ with a 20.256(3), b 22.418(6), c 20.433(5) Å, β 112.64(2)°, V 8564(4) Å^3, and $Z = 8$. Diffraction data were collected on a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo-K_α radiation, and the structure was refined to R_F 4.76% and R_{wF} 5.25% for the 8,847 independent reflections with $F_0 > 6\sigma(F_0)$. The structure consists of a triangular array of Ru atoms with seven terminal carbonyl ligands, three bridging diphenylphosphido ligands which bridge each of the Ru–Ru bonds, and the hydride ligand which bridges one Ru–Ru bond. Complex IV was also shown to give V upon photolysis and is thus an intermediate in the photoinduced formation of V from I.

There is an increasing interest in the chemistry of phosphido-, arsenido-, and sulfido-bridged compounds since such ligands inhibit the fragmentation tendencies of polynuclear complexes and thus facilitate the search for bimetallic reactivity effects [1,2]. While a number of methods have been demonstrated for the preparation of such bridged compounds, most lead to incorporation of the bridging ligand during the initial synthesis of the polynuclear complex when the metal framework is established [3]. Few methods have been described for the introduction of these ligands into preformed polynuclear compounds [4].

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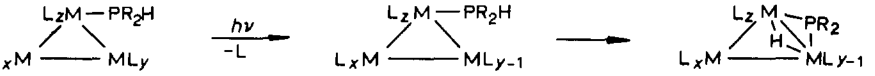
A method which has not been widely used but which would appear to have considerable generality for the introduction of phosphido-bridges involves the photolysis of PR_2H substituted compounds, as illustrated in eq. 1 [5].



(1)

Photolysis should lead to the formation of coordinatively-unsaturated metal centers, either via metal–metal bond cleavage or ligand loss [6], to which oxidative-addition of the P–H bond would give the phosphido-bridged derivative. This method in addition introduces the potentially useful hydride functionality. We illustrate herein the use of this method for the preparation of new phosphido-bridged clusters derived from $Ru_3(CO)_9(PPh_2H)_3$ (I).

Experimental

$Ru_3(CO)_{12}$ was prepared according to published procedures [7]. PPh_2H was obtained from Strem Chemical Co. and used without further purification. Solvents were dried by standard methods, and all reactions were conducted under a prepurified N_2 atmosphere using standard Schlenk techniques. IR spectra were recorded on a Perkin–Elmer 580 grating IR spectrophotometer using 0.5 mm NaCl solution IR cells. NMR spectra were recorded on a Bruker WP-200 FT NMR spectrometer. ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4 with downfield chemical shifts reported as positive. All ^1H NMR chemical shifts are relative to TMS. Electron impact mass spectra were recorded on an AEI-MS9 mass spectrometer operated in the electron impact mode with a source voltage of 70 eV and probe temperatures in the 100–200°C range. Field desorption mass spectra were recorded on a MAT 730 mass spectrometer by Dr. Thomas Criswell at the Eastman Kodak Research Laboratories, Rochester, New York. All photolyses were conducted in pyrex Schlenk vessels, or in a pyrex preparative-scale photochemical apparatus using a Hanovia 450 W medium-pressure Hg discharge lamp. Photolyses under H_2 pressure were conducted in a Fischer-Porter glass pressure reaction vessel (Lab-Crest Scientific, Warminster, PA). Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, NY.

Preparation of $Ru_3(CO)_9(PPh_2H)_3$ (I)

PPh_2H (0.51 ml, 2.92 mmol) was added to a hexane (75 ml) solution of $Ru_3(CO)_{12}$ (0.622 g, 0.973 mmol). This solution was stirred under N_2 for 12 h at 45°C during which time it darkened in color and a dark red precipitate formed. The precipitate was collected by filtration and washed with hexane until the washings were colorless. $Ru_3(CO)_9(PPh_2H)_3$ was thus obtained as a red powder in 70% yield (0.756 g, 0.679 mmol). Anal. Found: C, 48.59; H, 3.19; P, 8.24. $C_{45}H_{33}O_9P_3Ru_3$ calcd.: C, 48.43; H, 2.96; P, 8.33%. IR (KBr): ν(CO) 2045w, 1970s, br 1935s; ν(P–H) 2310m. UV/VIS: λ_{max} (benzene), 463 nm (ε 10,510 M^{-1} cm^{-1}).

Photolysis of I

Irradiation of benzene solutions of I with pyrex-filtered light ($\lambda \geq 300$ nm) results in a gradual color change from dark-red to golden yellow. Chromatography of the irradiated solution on silica gel using 30% CH_2Cl_2/70% hexane as the eluant gives separation of two fractions. The minor fraction and first to elute is yellow and contains a mixture of $Ru_2(\mu\text{-}PPh_2)_2(CO)_6$ (II) and $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8$ (III). The major second fraction is orange and contains a mixture of $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_7(PPh_2H)$ (IV) and $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ (V). Further attempts to separate these fractions by extensive chromatography or fractional crystallization were largely unsuccessful, although a crystalline sample of V was obtained by allowing a concentrated hexane solution of V to sit overnight at 0°C. A relatively pure (by spectroscopic data) sample of III was obtained in an experiment following chromatography of a solution of I irradiated under an H_2 atmosphere. Although the relative yields of II → V depend on the experimental conditions employed (see Results), in a typical experiment photolysis of a solution containing 0.1070 g (9.6×10^{-2} mmol) of I in 50 ml of benzene gave 0.0165 g of the II/III mixture and 0.0730 g of the IV/V mixture.

X-ray structure determination of $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ (V)

A rectangular red translucent crystal of V of dimensions $0.3 \times 0.4 \times 0.8$ mm, obtained as described above, was mounted and aligned on the Syntex $P2_1$ diffractometer at SUNY-Buffalo. Intensity data were collected as described previously [8]. Details are given in Table 1. All data were converted to $|F_o|$ values following correction for absorption, Lorentz and polarization factors. Any reflection with

TABLE 1

EXPERIMENTAL DATA FOR THE X-RAY DIFFRACTION STUDY OF $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ (V)

Crystal parameters at 21°C [a]

Crystal system: monoclinic
Space group: $P2_1/n$ [C_{2h}^5; No. 14]
a 20.256(3) Å
b 22.418(6) Å
c 20.433(5) Å
β 112.64(2)°

V 8564(4) $Å^3$
$Z = 8$
Mol. wt. = 1055.9
ρ(calcd) 1.64 g cm^{-3}
μ(Mo-K_α) 11.5 cm^{-1}

Measurement of data

Diffractometer: Syntex $P2_1$
Radiation: Mo-K_α ($\bar{\lambda}$ 0.71073 Å)
Monochromator: highly oriented graphite, equatorial mode ($2\theta_{mono}$ 12.2°)
Reflctns. measd.: $h, k, \pm l$
2θ range: 4.0–45.0°
Scan type: θ(crystal)–2θ(counter)
Scan width: $[2\theta(K_{\alpha_1}) - 1.0]$–$[2\theta(K_{\alpha_2}) + 1.0]$°
Scan speed: 4.0°/min in (2θ)
Bkgd. meast.: stationary crystal and counter at beginning and end of 2θscan, each for one quarter of the scan time
Reflctns. collected: 11630 total, merged to 10566 independent reflections
Std. reflctns.: three measured after each 97 reflctns. (1000; 0100; 0010); no decay was observed over the period of data collection

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[a] Unit cell parameters were derived by a least-squares fit to the setting angles of the unresolved Mo-$K_{\bar{\alpha}}$ components of 25 reflections with 2θ between 20 and 30°.

I(net) < 0 was assigned a value of $|F_o| = 0$. All calculations were performed on the CDC Cyber 730 computer at the Computer Center at SUNY-Buffalo. The structure was solved and refined with the use of MULTAN 76 [9] and SHELX 76 [10].

There are two molecules of $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7$ in the crystallographic asymmetric unit. Individual positional parameters of ruthenium and phosphorus atoms and atoms of the carbonyl groups were refined; phenyl rings were treated as rigid groups of D_{6h} symmetry with C–C 1.395 Å and C–C–C 120°. Anisotropic thermal parameters were used for Ru and P atoms; isotropic thermal parameters were used for all other atoms. The hydride ligands were located and refined; hydrogen atoms of the phenyl groups could not be incorporated because of program limitations. (There are 57 atoms per molecule - 114 atoms total - excluding the 60 phenyl hydrogens.)

TABLE 2

POSITIONAL PARAMETERS (AND E.S.D.'S) FOR $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7$ (V)

Atom	x	y	z	U_{iso}
Molecule A				
Ru(1)	0.09320(3)	0.27670(3)	0.51574(3)	
Ru(2)	0.01687(3)	0.17056(3)	0.53758(3)	
Ru(3)	0.08493(3)	0.24669(3)	0.65369(3)	
P(12)	−0.02665(11)	0.24279(10)	0.45008(11)	
P(13)	0.06300(12)	0.33867(10)	0.59776(11)	
P(23)	0.10784(11)	0.14561(9)	0.64514(10)	
O(1)	0.0955(4)	0.3771(4)	0.4170(4)	0.093(2)
O(2)	0.1433(4)	0.1786(3)	0.4423(4)	0.073(2)
O(3)	0.2509(4)	0.2819(3)	0.6167(4)	0.081(2)
O(4)	0.0365(4)	0.0730(4)	0.4448(4)	0.083(2)
O(5)	−0.1062(4)	0.1001(4)	0.5448(4)	0.089(2)
O(6)	0.2246(4)	0.2861(3)	0.7669(3)	0.072(2)
O(7)	0.0230(3)	0.2528(3)	0.7647(3)	0.065(2)
C(1)	0.0933(5)	0.3387(5)	0.4551(5)	0.063(3)
C(2)	0.1225(5)	0.2145(4)	0.4713(4)	0.048(2)
C(3)	0.1902(5)	0.2810(4)	0.5806(5)	0.055(2)
C(4)	0.0295(5)	0.1114(4)	0.4792(5)	0.054(2)
C(5)	−0.0588(5)	0.1280(4)	0.5409(5)	0.057(2)
C(6)	0.1724(4)	0.2704(4)	0.7228(4)	0.047(2)
C(7)	0.0472(4)	0.2506(4)	0.7226(4)	0.044(2)
C(8) [a]	−0.1047(3)	0.2885(3)	0.4359(3)	0.054(2)
C(9)	−0.1081	0.3469	0.4111	0.085(3)
C(10)	−0.1700	0.3806	0.3966	0.107(4)
C(11)	−0.2286	0.3560	0.4068	0.091(4)
C(12)	−0.2252	0.2976	0.4315	0.094(4)
C(13)	−0.1633	0.2638	0.4461	0.066(3)
C(14) [a]	−0.0460(3)	0.2188(3)	0.3584(2)	0.048(2)
C(15)	−0.1012	0.1779	0.3276	0.061(2)
C(16)	−0.1187	0.1595	0.2577	0.074(3)
C(17)	−0.0811	0.1821	0.2185	0.074(3)
C(18)	−0.0259	0.2230	0.2493	0.085(3)
C(19)	−0.0083	0.2414	0.3193	0.066(3)
C(20) [a]	0.1296(3)	0.3966(3)	0.6435(3)	0.049(2)

TABLE 2 (continued)

Atom	x	y	z	U_{iso}
C(21)	0.1807	0.4170	0.6186	0.060(3)
C(22)	0.2312	0.4592	0.6575	0.079(3)
C(23)	0.2307	0.4809	0.7212	0.081(3)
C(24)	0.1796	0.4604	0.7461	0.083(3)
C(25)	0.1290	0.4183	0.7072	0.067(3)
C(26) [a]	−0.0198(3)	0.3803(3)	0.5790(3)	0.052(2)
C(27)	−0.0252	0.4402	0.5585	0.094(4)
C(28)	−0.0863	0.4728	0.5514	0.118(5)
C(29)	−0.1421	0.4456	0.5642	0.103(4)
C(30)	−0.1368	0.3858	0.5844	0.078(3)
C(31)	−0.0757	0.3532	0.5918	0.052(2)
C(32) [a]	0.1976(3)	0.1257(3)	0.6515(3)	0.044(2)
C(33)	0.2088	0.0955	0.5970	0.066(3)
C(34)	0.2783	0.0868	0.6003	0.085(3)
C(35)	0.3365	0.1082	0.6582	0.096(4)
C(36)	0.3253	0.1384	0.7128	0.095(4)
C(37)	0.2558	0.1472	0.7094	0.075(3)
C(38) [a]	0.0900(3)	0.0901(2)	0.7024(2)	0.037(2)
C(39)	0.0661	0.0334	0.6757	0.055(2)
C(40)	0.0525	−0.0091	0.7188	0.066(3)
C(41)	0.0627	0.0051	0.7885	0.061(3)
C(42)	0.0866	0.0618	0.8152	0.059(2)
C(43)	0.1003	0.1043	0.7721	0.045(2)
H	−0.0039(37)	0.2335(32)	0.5891(35)	0.052(21)
Molecule B				
Ru(1)	0.30867(3)	0.21776(3)	0.39511(3)	
Ru(2)	0.40938(3)	0.14134(3)	0.35806(3)	
Ru(3)	0.46686(3)	0.24362(3)	0.43860(3)	
P(12)	0.29868(10)	0.17688(9)	0.28325(10)	
P(13)	0.37047(11)	0.30701(9)	0.38692(10)	
P(23)	0.50757(11)	0.14553(9)	0.46661(10)	
O(1)	0.1633(4)	0.2756(3)	0.3321(3)	0.073(2)
O(2)	0.2647(4)	0.0949(3)	0.4300(3)	0.069(2)
O(3)	0.3521(4)	0.2440(3)	0.5533(4)	0.084(2)
O(4)	0.3531(3)	0.0178(3)	0.3633(3)	0.057(2)
O(5)	0.4776(3)	0.0947(3)	0.2617(3)	0.072(2)
O(6)	0.5133(4)	0.2902(3)	0.5883(4)	0.078(2)
O(7)	0.5885(4)	0.3096(3)	0.4243(3)	0.073(2)
C(1)	0.2183(4)	0.2534(4)	0.3569(4)	0.047(2)
C(2)	0.2821(5)	0.1402(4)	0.4154(4)	0.050(2)
C(3)	0.3371(5)	0.2359(4)	0.4922(5)	0.056(2)
C(4)	0.3753(4)	0.0650(4)	0.3625(4)	0.038(2)
C(5)	0.4505(4)	0.1122(4)	0.2981(4)	0.042(2)
C(6)	0.4947(5)	0.2728(4)	0.5307(4)	0.049(2)
C(7)	0.5411(4)	0.2842(4)	0.4301(4)	0.045(3)
C(8) [a]	0.2838(3)	0.2216(2)	0.2045(2)	0.035(2)
C(9)	0.3420	0.2429	0.1910	0.043(2)
C(10)	0.3307	0.2752	0.1292	0.055(2)
C(11)	0.2612	0.2860	0.0809	0.057(2)
C(12)	0.2030	0.2647	0.0943	0.059(3)
C(13)	0.2142	0.2325	0.1561	0.047(2)

TABLE 2 (continued)

Atom	x	y	z	U_{iso}
C(14) [a]	0.2278(3)	0.1214(2)	0.2445(3)	0.041(2)
C(15)	0.2390	0.0770	0.2020	0.058(3)
C(16)	0.1862	0.0344	0.1701	0.077(3)
C(17)	0.1221	0.0362	0.1806	0.090(4)
C(18)	0.1108	0.0806	0.2229	0.093(4)
C(19)	0.1637	0.1232	0.2549	0.065(3)
C(20) [a]	0.3615(3)	0.3690(2)	0.4415(3)	0.046(2)
C(21)	0.2973	0.3792	0.4500	0.068(3)
C(22)	0.2910	0.4278	0.4897	0.081(3)
C(23)	0.3488	0.4663	0.5210	0.083(3)
C(24)	0.4130	0.4561	0.5126	0.087(3)
C(25)	0.4193	0.4074	0.4728	0.069(3)
C(26) [a]	0.3519(3)	0.3482(2)	0.3048(2)	0.038(2)
C(27)	0.4092	0.3650	0.2870	0.047(2)
C(28)	0.3975	0.4011	0.2280	0.063(3)
C(29)	0.3284	0.4205	0.1868	0.072(3)
C(30)	0.2711	0.4038	0.2046	0.065(3)
C(31)	0.2829	0.3676	0.2636	0.050(2)
C(32) [a]	0.5100(3)	0.1110(2)	0.5492(2)	0.035(2)
C(33)	0.5540	0.1363	0.6137	0.055(2)
C(34)	0.5581	0.1106	0.6773	0.060(3)
C(35)	0.5183	0.0597	0.6765	0.054(2)
C(36)	0.4743	0.0344	0.6120	0.051(2)
C(37)	0.4702	0.0601	0.5484	0.045(2)
C(38) [a]	0.5940(2)	0.1239(2)	0.4633(3)	0.035(2)
C(39)	0.6363	0.0789	0.5064	0.044(2)
C(40)	0.6975	0.0596	0.4969	0.053(2)
C(41)	0.7163	0.0852	0.4443	0.061(3)
C(42)	0.6739	0.1302	0.4012	0.057(2)
C(43)	0.6127	0.1495	0.4107	0.044(2)
H	0.4350(33)	0.2160(29)	0.3497(31)	0.028(18)

[a] First of six carbon atoms defining a rigid phenyl group of D_{6h} symmetry.

Refinement by 101-parameter cascade blocked matrix least-squares, converged with R_F 5.76% and R_{wF} 5.82% for all 10,566 independent reflections and R_F 4.76% and R_{wF} 5.25% for those 8,847 reflections with $F_o > 6\sigma(F_o)$. A final difference Fourier synthesis showed no significant peaks except for some of the hydrogen atoms associated with the phenyl ring carbon atoms. The analytical form [11a] of the scattering factors for neutral atoms were used throughout the analysis; both $\Delta f'$ and $i\Delta f''$ terms [11b] were included for all atoms. Positional parameters are given in Table 2. Tables of anisotropic thermal parameters, full lists of bond lengths and angles, and the structure factors are available from the author (G.L.G.) upon request.

Results

Preparation and characterization of $Ru_3(CO)_9(PPh_2H)_3$ (I)

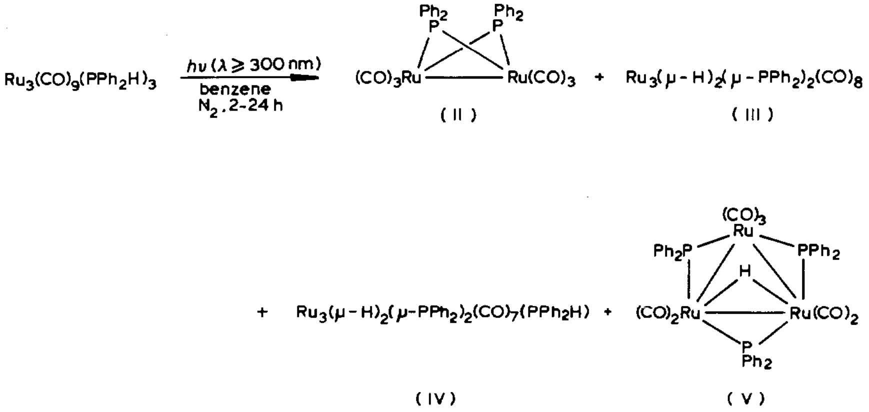
The reaction of $Ru_3(CO)_{12}$ with tertiary phosphines generally leads to the selective formation of trisubstituted derivatives, $Ru_3(CO)_9(PR_3)_3$ [12,13], and such is also the case with PPh_2H. When $Ru_3(CO)_{12}$ was stirred at 45°C with 3 equivalents of PPh_2H, the trisubstituted cluster I was isolated as a red powder in 70% yield, eq. 2.

$$\mathrm{Ru_3(CO)_{12} + 3PPh_2H \xrightarrow[\text{hexane}]{45°\text{C},\ 12\ \text{h}} \underset{(\text{I},\ 70\%)}{Ru_3(CO)_9(PPh_2H)_3} + 3CO} \tag{2}$$

This particular $Ru_3(CO)_9(PR_3)_3$ derivative has apparently not been previously reported. It was characterized by a satisfactory C, H, P analysis and by its field desorption mass spectrum which showed a parent ion at m/e 1115. Furthermore, its IR and UV/VIS spectra compare reasonably well to those of $Ru_3(CO)_9(PPh_3)_3$. For example, I shows three IR bands at 2045w, 1970s, br and 1935s, br, cm^{-1} which are similar in pattern to the three bands of $Ru_3(CO)_9(PPh_3)_3$ at 2044vw, 1978(sh), and 1967s, br cm^{-1} [14]. The UV/VIS absorption maximum of I is at 463 nm with ε 10,510 l mol^{-1} cm^{-1} compared to the principal absorption feature of $Ru_3(CO)_9(PPh_3)_3$ at λ_{max} 508 nm (ε 12,390 l mol^{-1} cm^{-1}) [15]. Complex I also shows a medium intensity P–H stretch at 2310 cm^{-1} in its IR spectrum. Although the structure of $Ru_3(CO)_9(PPh_2H)_3$ is not known with certainty, it is likely to have the same structure believed to be adopted by other $Ru_3(CO)_9(PR_3)_3$ derivatives with one PR_3 ligand coordinated to each Ru [14,16].

Photochemistry of I

Photolysis of benzene solutions of $Ru_3(CO)_9(PPh_2H)_3$ leads to a mixture of four products which can be partially separated by chromatography and fractional crystallization (See Experimental), eq. 3. Of these IV and V constitute ~90% of the product mixture with II and III formed in relatively minor amounts.



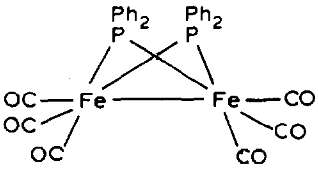
(3)

Compounds II and III elute together upon SiO_2 chromatography as do IV and V. Extensive chromatography of these fractions using various supports and solvent mixtures did not lead to their further separation, although small amounts of relatively pure III and V were obtained by fractional crystallization of their respective mixtures (see Experimental).

The ratio of the products II → V is variable, depending upon irradiation time and experimental conditions. In a typical experiment in which a ~ 10^{-3} M benzene solution of $Ru_3(CO)_9(PPh_2H)_3$ was irradiated for 4–5 h, the relative spectroscopic yields of II → V were approximately 4, 5, 72, and 19%, respectively. The relative yields of II and III do not depend markedly upon irradiation time but IV converts into V with increasing time of irradiation. For example, when the reaction was monitored by ^{1}H NMR spectroscopy, integration of the spectrum recorded after 2 h irradiation showed the ratio of IV to V to be 4.5 and after 4.5, 23 and 62 h irradiation times, the IV/V ratios are 1.7, 0.7, and 0.6, respectively. In separate photolysis experiments beginning with the IV/V mixture, ^{1}H NMR monitoring showed the photoinduced IV → V conversion to be clean with no evidence for products other than V. When photolysis is conducted under H_2 rather than an N_2 atmosphere, the yield of III increases significantly relative to that of II, IV, and V. For example, after 3 h irradiation of ~ 10^{-3} M $Ru_3(CO)_9(PPh_2H)_3$ solutions under H_2, the relative yields of II → V are 3, 17, 68 and 12%, respectively.

Characterization of $Ru_2(\mu\text{-}PPh_2)_2(CO)_6$, (II) and $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8$ (III)

It has not proven possible to separate II and III by chromatographic techniques and a pure sample of II cannot be obtained by this procedure. However, complex II has been independently prepared and characterized by Stone and co-workers [9]. The IR bands at 2072s, 2041s, 2011s, 2007sh, 1983s, and 1975s cm^{-1} reported for this complex are clearly observable in the mixture of II and III prepared by photolysis of $Ru_3(CO)_9(PPh_2H)_3$. ^{31}P NMR data for II have not been previously reported, but the ^{31}P{^{1}H} NMR spectrum of a mixture of II and III shows only two singlets at δ 164.1 and 110.9 which are respectively assigned III and II. The δ 110.9 singlet does not split in the proton-coupled ^{31}P NMR spectrum, consistent with its assignment to II which has no hydrides. The highest mass peak observed in the electron impact (EI) mass spectrum of the mixture of II/III was at m/e 742, corresponding to the parent ion of II. Also observed were fragment ions corresponding to successive loss of the 6 carbonyl ligands. Complex III does not interfere with this analysis since it is not sufficiently volatile to give an EI mass spectrum under these conditions. The structure of II has not been determined by X-ray diffraction although that of its isoelectronic Fe analog VI has [17]. The latter has the bent structure drawn below with a pseudo-octahedral coordination geometry about each

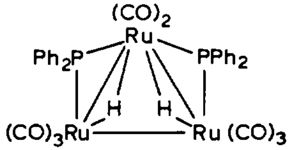


(VI)

Fe [17]. The structure of II is probably similar to that of VI.

The highest mass peak in the field desorption (FD) mass spectrum of the II/III mixture was at m/e 899 consistent with the $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_8$ formulation given to III. The ^{1}H and ^{31}P NMR spectra of the II/III mixture are also consistent with such a formulation. Thus the δ 164.1 singlet in the ^{31}P{^{1}H} NMR spectrum splits into a 1/2/1 triplet with $J(^{31}P-^1H)$ 23 Hz in the proton-coupled ^{31}P NMR spectrum, implying the presence of two equivalent hydrides. The ^{1}H NMR spectrum of the II/III mixture shows only one triplet in the hydride region at δ -16.2 with $J(^1H-^{31}P)$ 23 Hz, matching the coupling observed in the ^{31}P NMR spectrum. The triplet pattern implies the presence of two phosphorus nuclei in III. Also, the downfield position of the ^{31}P NMR resonance of III is consistent with these phosphorus ligands being μ-PPh$_2$ groups bridging two metals joined by a metal–metal bond. [1a,18]. A very small amount of an apparently pure sample of III was obtained in a single fractional crystallization experiment and the IR spectrum of this sample in hexane solution in the 2200–1500 cm^{-1} region showed only terminal ν(CO) bands at 2079m, 2044s, 2028m, 2016m, 1988m, and 1975m. These bands are also evident in the IR spectrum of the II/III mixture.

Although several reasonable structures can be drawn for III which fit the 18-valence electron rule and the spectroscopic data, we believe the most likely structure to be that sketched in IIIa below.

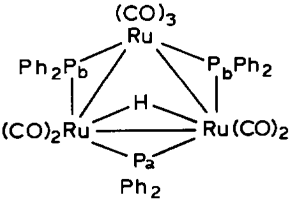


(IIIa)

The Fe analog of III with μ-PMe$_2$ ligands has been prepared. Its structure was found by Vahrenkamp and coworkers [19] to be analogous to that sketched above. Although the two hydrides and the two μ-PPh$_2$ ligands of IIIa are chemically equivalent, they are not magnetically equivalent. For IIIa to be consistent with the ^{1}H and ^{31}P NMR data, the protons have to either be rapidly exchanging positions on the NMR time-scales or the $J(^1\text{H}-^{31}\text{P})$ coupling constants have to be of similar magnitude.

Spectroscopic characterization of $Ru_3(\mu\text{-}H)_2(\mu\text{-}PPh_2)_2(CO)_7(PPh_2H)$ *(IV) and* $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ *(V)*

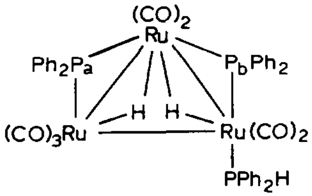
A crystalline sample of pure V was obtained by concentration of a hexane solution of the IV/V mixture from an exhaustively irradiated sample of Ru$_3$(CO)$_9$(PPh$_2$H)$_3$. As noted above, such solution should be relatively rich in V as compared to IV. Complex V was fully characterized by a single crystal X-ray diffraction study (vide infra) and has the structure sketched below.



(V)

The ^{1}H NMR spectrum of V in the metal-hydride region shows a doublet of triplets at δ −16.6 ($J(^{31}\text{P}-^1\text{H})$ 21 and 15 Hz), implying coupling to two equivalent and one non-equivalent phosphorus nuclei, consistent with the solid state structure. The ^{31}P{^{1}H} NMR spectrum of V shows an AB$_2$ pattern with resonances centered at δ 178.0 and 159.8 with $J(^{31}\text{P}_a-^{31}\text{P}_b)$ 120.5 Hz and $J/\Delta\nu = 0.082$, also consistent with the solid state structure. The IR spectrum of V shows in the 2200–1500 cm^{-1} region only terminal ν(CO) bands at 2056m, 2040m, 2017s, 1983s, and 1958m, br cm^{-1}. A parent ion at m/e 1058 is also apparent in its field desorption mass spectrum.

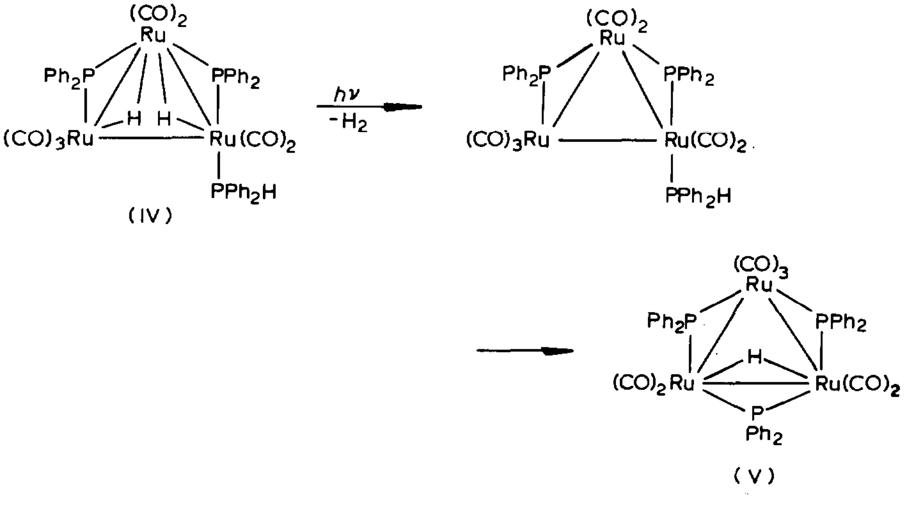
The ^{1}H and ^{31}P NMR spectra of the IV/V mixture also shows resonances which can be attributed to IV and are consistent with the structure drawn below.



(IV)

Three sets of resonances are seen in the ^{31}P{^{1}H} NMR spectrum at δ 166.4 d ($J(^{31}P-^{31}P)$ 103.4 Hz), δ 161.4 dd ($J(^{31}P-^{31}P)$ 103.4 and 17.0 Hz), and δ 25.0 d ($J(^{31}P-^{31}P)$ 17.0 Hz), in addition to resonances due to V. The two downfield resonances are in the region generally associated with μ-PPh$_2$ ligands which bridge two metals joined by a metal–metal bond [1a,18] and are assigned to P$_a$ and P$_b$, respectively. Upon proton-coupling the δ 25.0 resonance splits into a broad doublet with $J(^{31}P-^1H) \approx 362$ Hz, consistent with its assignment to a PPh$_2$H ligand with a direct P–H bond. The proton resonance of the PPh$_2$H ligand appears at δ 5.5 with $J(^{31}P-^1H)$ 365 Hz. The ^{1}H NMR spectrum of IV in the metal hydride region shows two equal intensity ddd resonance patterns at δ -15.6 ($J(^1H-^{31}P)$ 26.0, 20.9, and 4.5 Hz) and δ -16.6 ($J(^1H-^{31}P)$ 24.6, 21.2, and 4.4 Hz). That these two resonance patterns are due to two nonequivalent hydrides was shown by observing an increased Hz separation between them when the spectrum was recorded on a higher-field instrument.

Although the structure of IV is not known with certainty, that drawn above is consistent with the NMR data. Such a structure is also consistent with the observed photoinduced IV → V transformation. Photoinduced loss of H$_2$ from IV followed by oxidative-addition of the P–H bond across the open coordination site would lead



(4)

directly to V, eq. 4. Although it does not seem as likely, H_2 loss in the IV → V conversion could also occur via direct coupling of one of the original hydrides with the PPh_2H hydrogen.

Crystal and molecular structure of $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ (V)

ORTEP drawings of the two crystallographically-independent molecules of V are

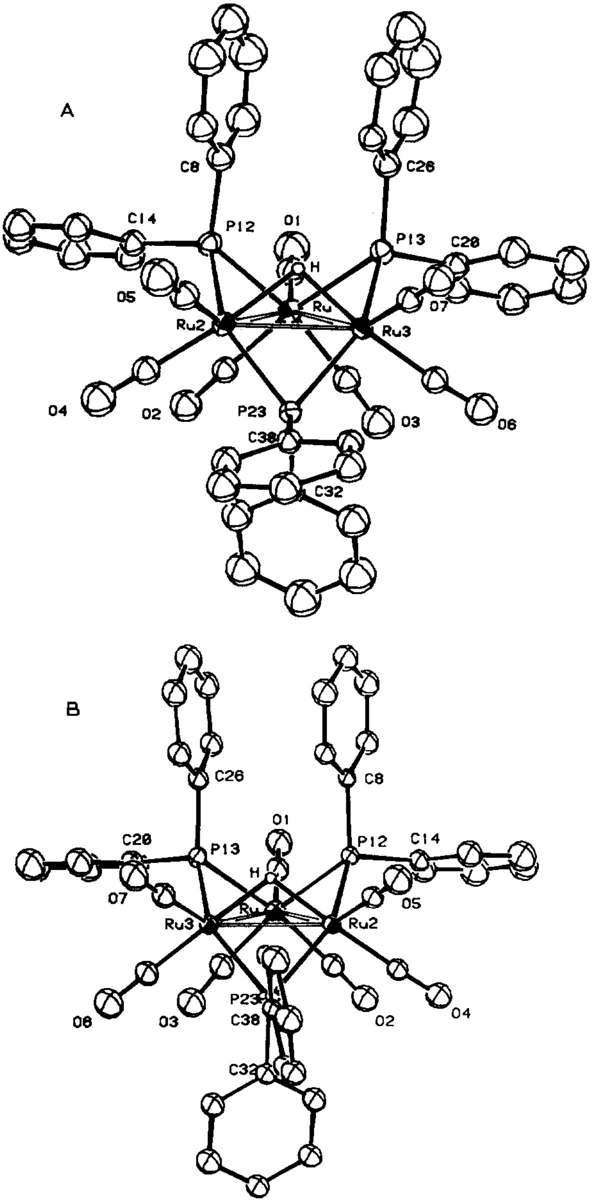


Fig. 1. Stereochemistry of the two independent molecules of $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7$ (V). (A) Molecule A, (B) Molecule B. Note that the molecules differ principally only by the rotation of the phenyl group about the P(23)–C(38) bond. Each molecule has approximate C_s symmetry.

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) FOR $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7$ (V)

	Molecule A	Molecule B
Metal-metal distances		
Ru(1)-Ru(2)	2.964(1)	2.977(1)
Ru(1)-Ru(3)	2.965(1)	3.033(1)
Ru(2)-Ru(3)	2.814(1)	2.801(1)
Metal-phosphorus distances		
Ru(1)-P(12)	2.400(3)	2.398(2)
Ru(1)-P(13)	2.430(2)	2.400(2)
Ru(2)-P(12)	2.320(2)	2.315(2)
Ru(2)-P(23)	2.327(2)	2.342(2)
Ru(3)-P(13)	2.316(2)	2.314(2)
Ru(3)-P(23)	2.333(2)	2.341(2)
Metal-hydride (bridging) distances		
Ru(2)-H	1.90(8)	1.78(7)
Ru(3)-H	1.80(6)	1.79(6)

shown in Fig. 1. The principal difference between the two molecules involves a rotation (by about $\pi/2$ radians) of the phenyl ring about its C(38)-P(23) ipso linkage. Relevant interatomic distances and angles of the two molecules are collected in Tables 3 and 4 respectively. There are three terminal carbonyl ligands bound to

TABLE 4

SELECTED INTERATOMIC ANGLES (°) FOR $Ru_3(\mu\text{-H})(\mu\text{-PPh}_2)_3(CO)_7$ (V)

	Molecule A	Molcule B
Intermetallic angles		
Ru(3)-Ru(1)-Ru(2)	56.7	55.5
Ru(3)-Ru(2)-Ru(1)	61.7	63.2
Ru(2)-Ru(3)-Ru(1)	61.6	61.2
Ru-P-Ru angles		
Ru(1)-P(12)-Ru(2)	77.8(1)	78.3(1)
Ru(1)-P(13)-Ru(3)	77.3(1)	80.1(1)
Ru(2)-P(23)-Ru(3)	74.3(1)	73.5(1)
Ru-H-Ru angles		
Ru(2)-H-Ru(3)	99(4)	104(3)
P-Ru-H (hydride) angles		
P(12)-Ru(2)-H	79.0(21)	81.8(18)
P(23)-Ru(2)-H	85.4(18)	83.1(16)
P(13)-Ru(3)-H	80.6(23)	80.7(20)
P(23)-Ru(3)-H	87.6(23)	83.0(20)
Ru-Ru-H angles		
Ru(3)-Ru(2)-H	39.2(19)	38.3(20)
Ru(2)-Ru(3)-H	41.9(25)	38.2(22)

Ru(1) and two each to Ru(2) and Ru(3). In addition, the three diphenylphospido ligands bridge each of the Ru–Ru bonds, occupying a diagonal position midway between axial and equatorial. The hydride ligands, which were located and refined, occupy similar positions about the Ru(2)–Ru(3) bonds.

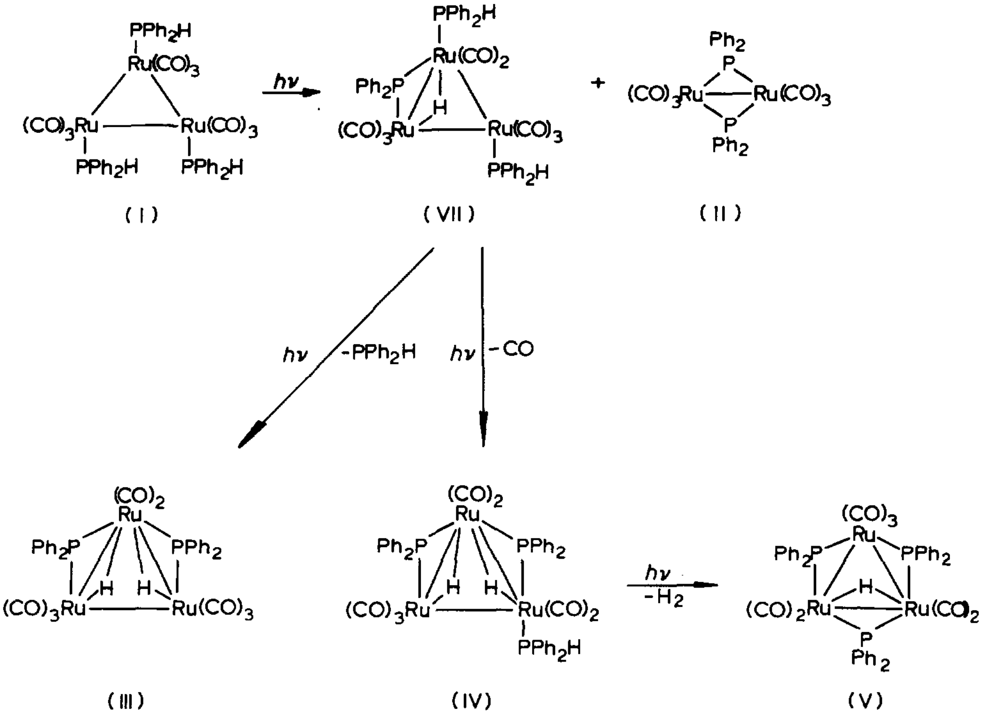
The Ru(1)–Ru(2) and Ru(1)–Ru(3) bonds, which are bridged only by single diphenylphosphido ligands, have lengths ranging from 2.964(1) through 3.033(1) Å. In contrast to this, the Ru(2)–Ru(3) bonds, which are bridged both by diphenylphosphido and hydride ligands, have lengths of only 2.814(1) and 2.801(1) Å. Relative to the parent compound, $Ru_3(CO)_{12}$, in which Ru–Ru(ave) 2.854 Å [20], the former bonds are substantially lengthened and the latter are substantially shortened. A very similar situation has recently been observed in the species $Ru_3(\mu\text{-}H)_2(CO)_6(\mu\text{-}PPhCH_2PPh_2)_2$ [21]; here, however, there is some disorder of the hydride site. The $(\mu\text{-}H)(\mu\text{-}PPh_2)$ bridged Ru–Ru distance may also be compared to the $(\mu\text{-}H)(\mu\text{-}X)$ bridged Os–Os distances determined for a variety of $Os_3(\mu\text{-}H)(\mu\text{-}L)(CO)_{10}$ molecules, and which are summarized in ref. 22.

The Ru–P distances for the phosphorus atoms which are *trans* to CO ligands (i.e., Ru(1)–P(12) and Ru(1)–P(13) linkages) range from 2.398(2) through 2.430(2) Å and are substantially longer then the remaining Ru–P distances (all of which are trans to diphenylphosphido ligands and range from 2.314(2) through 2.342(2) Å). All Ru–P–Ru angles are acute, but those spanning the hydrido-bridged Ru(2)–Ru(3) bonds are substantially more acute than the rest (viz., 73.5(1)–74.3(1)° versus 77.3(1)–80.1(1)°). Individual Ru–H distances range from 1.78(7) through 1.90(8) Å, with associated Ru(2)–H–Ru(3) angles of 99(4) and 104(3)°.

Discussion

The photochemistry of $Ru_3(CO)_9(PR_3)_3$ derivatives has not been clearly defined, although studies by Wrighton and co-workers [23] indicate that photoinduced metal–metal bond cleavage probably occurs in the primary photochemical event. It has been shown that eventual fragmentation of the trimeric complexes occurs subsequent to photolysis in the presence of excess PR_3, yielding mononuclear $Ru(CO)_3(PR_3)_2$ in a low quantum yield process [23b]. Although we did observe fragmentation to a small extent upon photolysis of $Ru_3(CO)_9(PPh_2H)_3$, as evidenced by the low-yield formation of II, net fragmentation is not a significant photochemical process for this compound, since the trinuclear framework is maintained in the major portion of the products.

We rationalize the formation of the observed photoproducts II → V by the overall mechanism shown in Scheme 1. Irradiation of I apparently can give net metal–metal bond cleavage with subsequent formation of II. Competing with this process must be photoinduced CO loss from I, followed by oxidative-addition of the P–H bond of a PPh_2H ligand to give an intermediate such as VII. Although VII was neither isolated nor characterized, a number of unassigned ^{31}P and ^{1}H NMR resonances are evident in the early stages of the photolysis reaction and then disappear as the concentration of the characterized products increases. Photoinduced loss of PPh_2H from VII followed by oxidative-addition of the P–H bond of the remaining PPh_2H ligand would result in the formation of complex III. Photoinduced carbon monoxide loss from VII followed by oxidative-addition of the P–H bond of one of the remaining

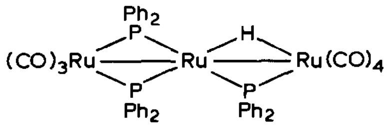


SCHEME 1

PPh_2H ligands would lead to complex IV, which upon prolonged irradiation leads to loss of H_2 and the formation of V.

It also seemed possible that complex IV could be an intermediate leading to III, since photoinduced substitution of CO for PPh_2H in IV would lead directly to III. However, this does not occur since photolysis under a CO atmosphere of a solution of a IV/V mixture that was rich in IV gave only V with no ^1H NMR evidence for the formation of III.

Finally, it should be noted that an open structure such as VIII is also consistent with the ^{31}P and ^1H NMR data obtained for V, but it is of course not the structure



(VIII)

determined by X-ray diffraction. However, rearrangement of V into VIII upon dissolution of solid samples cannot be ruled out by the present data, although such seems unlikely, especially since VIII is deficient by 2 electrons. However, a structure analogous to VIII has been suggested for the Fe analog of V, $Fe_3(\mu\text{-}H)(\mu\text{-}PPh_2)_3(CO)_7$ [24].

Acknowledgment

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