Table VI. Effective Softness Values of Metals

complexes	$E_n^\ddagger$(eff) of M	$E_n^\ddagger$(eff) of Hg
$CoHg(SCN)_4$	−3.21	−7.83
$(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$	−2.87	−7.49
$(MeOH)_2NiHg(SCN)_4$	−2.68	−7.69
$(MeOH)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$	−2.43	−7.32

softness values of the metal ions, ^-NCS, and ^-SCN and various ligands (L) have been calculated by the method reported elsewhere[13,14] and are presented in Table V as $E_n^\ddagger$ for metal ions and $E_m^\ddagger$ for thiocyanates and ligands. A higher value of difference ΔE_{nm} between the metal ion and the base indicates better match.[15] On the basis of this assumption the ligands (L) prefer linkage to cobalt or nickel. Similarly the N end of thiocyanate shows better match with cobalt and the S end with mercury. Various linkages shown in the proposed structures are consistent with this requirement of the HSAB principle.[16]

B. Ionic Complexes $[Co(phen)_3][C_6H_5Hg(SCN)_2]_2$, $[Co(bpy)_3][C_6H_5Hg(SCN)_2]_2$, $[Ni(phen)_2][C_6H_5Hg(SCN)_2]$, and $[Ni(bpy)_2][C_6H_5Hg(SCN)_2]_2$. These complexes are soluble in Me_2SO and have been crystallized from this solvent. Their molar conductance data as presented in Table III[5] indicate that they are 1:2 electrolytes. The electronic spectra and their spectral parameters and magnetic moments show that cobalt has octahedral coordination geometry and nickel is in a square-planar configuration. The presence of C–N stretching bands in the range 2080–2110 cm^{-1}, C–S stretching in the range 690–725 cm^{-1}, and NCS bending in the range 420–450 cm^{-1} is indicative of thiocyanate linkage through the S atom.

On the basis of these results it can be presumed that the cation consists of a metal ion duly coordinated with the ligand and can be represented by $[Ni(L\text{-}L)_2]^{2+}$ and $[Co(L\text{-}L)_3]^{2+}$. The possible anion is, therefore, $[C_6H_5Hg(SCN)_2]^-$. The coordination number of mercury in the anion is three presumably. Previous workers[17,18] have also reported mercury in tricoordinated state. The cation $[Co(L\text{-}L)_3]^{2+}$ will thus have O_h symmetry and $[Ni(L\text{-}L)_2]^{2+}$ D_{4h} symmetry. The anion $[C_6H_5Hg(SCN)_2]^-$ in both the cases will have C_{2v} symmetry. With assumption of these symmetries the number of infrared-active bands have been calculated and the results are given in Table IV[5] along with the observed number of bands. Both are in good agreement.

Comparison with Corresponding Bimetallic Tetrathiocyanates. (1) Bases like py, Amp, THF, DIOX, and Me_2SO form polymeric bridged complexes with $CoHg(SCN)_4$[19] and monomeric bridged complexes with the organobimetallic tetrathiocyanates. (2) bpy and phen form ionic complexes with $NiHg(SCN)_4{\cdot}2H_2O$ and $(C_2H_5OH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, but nickel forms octahedral cations with the former and square planar cations with the latter. (3) Soft donors like triphenylphosphine and ethylenethiourea form well-defined compounds of the type $(L)_2Co(NCS)_2Hg(SCN)_2$ (L = triphenylphosphine and ethylenethiourea) with $MHg(SCN)_4$.[20] The corresponding organobimetallic compounds do not react with these ligands. The calculation of effective softness values[14] of cobalt and nickel as presented in Table VI in both types of Lewis acid show that these metal ions become harder in the organobimetallic compounds. The increase in hardness might be the possible reason for their inactivity toward soft bases. (4) The organobimetallic compounds are comparatively more soluble in common organic solvents, and their molecular weights can be determined. Most of these complexes are crystalline, and the cobalt Lewis acid has a sharp melting point. The corresponding bimetallic tetrathiocyanates are generally insoluble solids, which have a broad decomposition range. (5) Singh and Srivastava[14] have reported a new method known as "matching constant" for deriving comparative stability in a set of related complexes. The results of matching constant calculations as presented in Table IV[5] indicate that the complexes of organobimetallic compounds are more stable than the complexes of bimetallic tetrathiocyanates. This appears reasonable because the THF complexes of bimetallic tetrathiocyanates lose their THF at room temperature, whereas the corresponding complex does not lose THF even on mild heating.

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Registry No. $(py)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-25-0; $(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-24-9; $(Nia)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-23-8; $(3\text{-}Amp)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-22-7; $(4\text{-}Amp)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-21-6; $(Me_2SO)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-20-5; $(THF)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-19-2; $(DIOX)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-18-1; $(phen)_3(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-17-0; $(bpy)_3(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-16-9; $(MeOH)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-15-8; $(EtOH)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-14-7; $(Me_2SO)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-13-6; $(THF)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77482-01-0; $(DIOX)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-12-5; $(py)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-11-4; $(Nia)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-10-3; $(Ani)_2(SCN)_2Ni(NCS)Hg_2(C_6H_5)_2$, 77462-09-0; $(4\text{-}Amp)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-08-9; $(phen)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77519-67-6; $(bpy)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77519-45-0; $Co(NCS)_2{\cdot}2py$, 15613-11-3; C_6H_5HgSCN, 16751-55-6; $Ni(NCS)_2{\cdot}4py$, 14724-08-4; $Ni(NCS)_2{\cdot}4Nia$, 63313-22-4; $Ni(NCS)_2{\cdot}4(4\text{-}Amp)$, 72804-72-9; $Ni(NCS)_2{\cdot}4Ani$, 14324-74-4.

Supplementary Material Available: Tables I–IV (analytical and IR and electronic spectral data) and the spectral traces of the IR (4000–200 cm^{-1}) and far-IR (450–50 cm^{-1}) for $(4\text{-}Amp)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Laboratoire de Chimie de Coordination du
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Oxidative-Addition Reaction of Bis(diphenylphosphino)methane with $Ru_3(CO)_{12}$. Formation of a "Capped" Phosphinidene Triruthenium Carbonyl Cluster

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Received October 22, 1980

Transition-metal clusters are the focus of considerable attention in view of catalysis.[1] However, their possible degradation under potentially interesting reaction conditions is an obstacle to proving cluster catalysis. This led several groups

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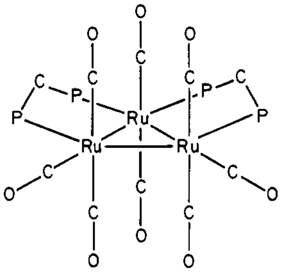
to design a new class of stabilized clusters involving a metal framework supported by nonfluxional bridging ligands.[2-5]

A new research program in this area led us to examine the efficiency of bis(diphenylphosphino)methane (dppm) as a stabilizing agent for $Ru_3(CO)_{12}$. Under mild conditions, the substituted derivative $Ru_3(CO)_8$ $(ddpm)_2$ (**1**) was isolated in good yield and characterized by X-ray diffraction.[6] Under more vigorous conditions, **1** was found to undergo a facile transformation via intramolecular oxidative cleavage of a coordinated dppm ligand, leading to the unexpected species $Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$ (**2**). A study of this reaction is reported there along with a complete X-ray structural analysis of the latter species **2**.



1

Experimental Section

Preparation of Complexes. Reactions were carried out under reflux with a dry-nitrogen atmosphere. $Ru_3(CO)_{12}$ was supplied by Johnson Mathey Chemicals. Organic solvents were degassed prior to use.

$Ru_3(CO)_8(dpm)_2$ (1). A xylene solution (15 mL) containing $Ru_3(CO)_{12}$ (250 mg, 0.391 mmol) and bis(diphenylphosphino)methane (300.68 mg, 782 mmol) was heated at 80–85 °C for 2 h. Development of an intense red color above 60 °C was indicative of complex formation. The solution was then cooled and evaporated to dryness.

The solid residue was extracted with 5 mL of acetone; 15 mL of ethanol was then added, and the solution was set aside for 1 h. Then 370 mg of red lozenge base parallelepipedic crystals was filtered and washed with ethanol (yield, 73%); the crystals were directly suitable for X-ray analysis.[6]

$Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$ (2). Compound **1** can be easily converted into **2** by mild pyrolysis above 100 °C in xylene. However, the simplest way to this species does not require the isolation of **1**. A xylene solution (10 mL) containing $Ru_3(CO)_{12}$ (100 mg, 0.156 mmol) and dppm (120 mg, 0.312 mmol) was heated at 80 °C for 1 h; the temperature was then raised to 130 °C for 3 h. The initial red color turned brown while a yellow crystalline precipitate appeared. The solution was then cooled and concentrated. The insolubility of the yellow compound in most solvents but dichloromethane allowed a clean separation of 78 mg of crystals (yield 42%). (Anal. Calcd: C, 51.47; H, 3.19; P, 10.41. Found: C, 52.45; H, 3.27; P, 10.07.)

IR Spectra. The IR spectra in the ν(CO) region were recorded on a Perkin-Elmer 225 spectrophotometer: $Ru_3(CO)_8(dppm)_2$ (ν(CO), cm^{-1}, CsBr pellets) 2040 (s), 1955 (br), 1890 (m); $Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$ (ν(CO), cm^{-1}, CsBr pellets) 2051 (s) 1990 (s), 1983 (s), 1968 (m), 1960 (m), 1938 (s), 1932 (s) (s = strong, m = medium, br = broad).

X-Ray Structural Analysis. Suitable crystals of **2** were grown from a 1/1 dichloromethane/heptane mixture. Preliminary Laue and precession photographs indicated orthorhombic symmetry with extinction patterns consistent with space group $P2_12_12_1$. The crystal was centered on a Nonius CAD-4 diffractometer. Unit cell parameters were obtained from a least-squares fit to the setting angles of the Mo Kα peaks of 25 high-angle reflections. These parameters are reported in Table I together with pertinent crystal data.

Table I. Crystal Data

formula	$Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$
fw	1189.09
a, Å	13.861 (4)
b, Å	13.754 (3)
c, Å	25.782 (7)
V, Å^3	4915.43
Z	4
d_{calcd}, g cm^{-3}	1.607
μ, cm^{-1}	10.70
crystal size, mm^3	0.012
radiation (λ, Å)	Mo Kα (0.7093) from monochromator
takeoff angle, deg	3
std reflctns	(4,0,13)–(168)
θ limits, deg	2.0–22.0
data collection	3412 reflctns; scan mode ω–2θ
unique data used	$2914 F_o^2 > 3\sigma(F_o^2)$
final no. of variables	292
weighted function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weight	$w = 4F_o^2/\sigma^2(F_o)^2$
convergence factors	$R_w = [\Sigma w^2(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w^2\lvert F_o\rvert^2]^{1/2}$; $R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$

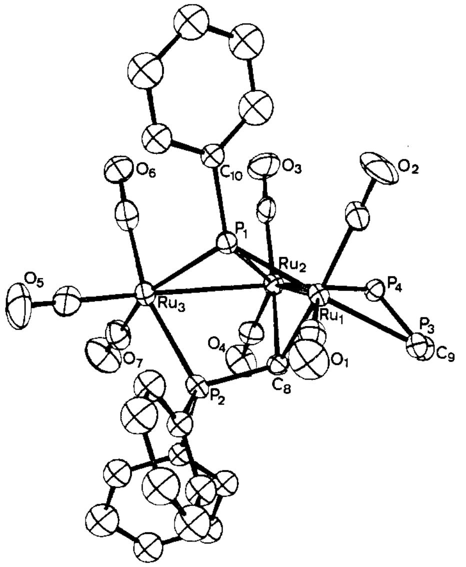


Figure 1. Geometry and labeling of the complex $Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$. The benzene rings of dppm ligand have been omitted for clarity.

Atomic scattering factors were taken from the usual tabulation;[7a] both the real and imaginary components of anomalous dispersion[7b] were included for ruthenium and phosphorus atoms. The structure was solved by standard Patterson and Fourier syntheses.[8] Refinement of an isotropic model converged to $R_w = 6.5$ and $R = 5.4$. Anisotropic thermal parameters were then used for 26 atoms, while benzene rings

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(6) Separate communication to be submitted to *Acta Crystallogr.* Crystal data: orthorhombic symmetry; space group $Pca2_1$; $a = 21.371$ (5) Å, $b = 15.655$ (2) Å, $c = 18.242$ (4) Å; $R_w = 0.050$.

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(8) All calculations were performed with the use of the CII Iris 80 computer of the Centre Interuniversitaire de Calcul de Toulouse. In addition to various local programs, modified versions of the following ones were used: Zalkin's FORDAP Fourier summation program; Ibers' NUCLS full-matrix least-squares program, which in its nongroup form resembles the Busing and Levy ORFLS program; Busing and Levy's ORFFE error function program; Johnson's ORTEP program.

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $Ru_3(CO)_7(P(C_6H_5))(CHP(C_6H_5)_2)(dppm)$[a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	0.30062 (6)	0.47022 (6)	0.35614 (3)	3.26 (5)	4.41 (6)	0.86 (1)	−0.30 (5)	−0.03 (2)	−0.13 (2)
Ru(2)	0.12409 (6)	0.55077 (6)	0.39224 (3)	3.48 (5)	3.98 (5)	1.00 (1)	−0.13 (5)	−0.12 (2)	−0.06 (2)
Ru(3)	0.22555 (7)	0.66486 (7)	0.46861 (3)	5.39 (6)	4.62 (6)	1.03 (1)	−0.35 (5)	−0.05 (3)	−0.37 (2)
P(1)	0.2792 (2)	0.6262 (2)	0.3852 (1)	4.5 (2)	4.3 (2)	0.99 (4)	−0.7 (2)	−0.08 (8)	−0.04 (8)
P(2)	0.2632 (2)	0.4997 (2)	0.48284 (10)	3.9 (2)	5.3 (2)	0.92 (4)	0.0 (1)	−0.17 (7)	−0.06 (7)
P(3)	0.2406 (2)	0.3209 (2)	0.3288 (1)	3.6 (2)	4.6 (2)	1.11 (4)	−0.1 (2)	0.02 (7)	−0.24 (8)
P(4)	0.0551 (2)	0.4398 (2)	0.3357 (1)	3.4 (2)	3.9 (2)	1.23 (5)	−0.2 (1)	−0.23 (7)	−0.08 (8)
C(1)	0.4225 (9)	0.4231 (9)	0.3708 (4)	5.9 (8)	6.6 (9)	1.4 (2)	−0.4 (8)	0.6 (4)	−0.2 (4)
O(1)	0.5002 (6)	0.3945 (7)	0.3782 (4)	4.9 (6)	11.9 (8)	2.7 (2)	2.1 (6)	−0.5 (3)	0.0 (3)
C(2)	0.3466 (8)	0.5107 (8)	0.2897 (4)	5.4 (8)	6.4 (8)	1.2 (2)	−0.9 (7)	0.0 (3)	−0.5 (4)
O(2)	0.3787 (7)	0.5352 (8)	0.2513 (3)	11.0 (7)	14.6 (9)	1.0 (1)	−3.5 (8)	1.2 (3)	1.0 (3)
C(3)	0.0610 (8)	0.6555 (9)	0.3589 (4)	5.9 (8)	5.1 (8)	1.5 (2)	−1.6 (7)	−0.4 (4)	−0.7 (4)
O(3)	0.0194 (7)	0.7174 (6)	0.3376 (4)	10.9 (8)	6.0 (6)	3.0 (2)	1.4 (6)	−1.6 (4)	1.1 (3)
C(4)	0.0279 (8)	0.5299 (9)	0.4435 (4)	4.4 (7)	5.9 (8)	1.5 (2)	0.2 (7)	−0.2 (3)	0.2 (4)
O(4)	−0.0323 (6)	0.5144 (7)	0.4732 (3)	5.4 (5)	12.2 (8)	1.8 (2)	−0.8 (6)	1.2 (3)	−0.1 (3)
C(5)	0.3299 (9)	0.7195 (9)	0.5078 (5)	6.1 (9)	6.7 (9)	1.8 (3)	−0.9 (8)	0.6 (4)	−0.3 (4)
O(5)	0.3892 (8)	0.7528 (8)	0.5321 (4)	10.5 (9)	13.0 (10)	3.0 (2)	−4.1 (8)	−1.6 (4)	−2.2 (4)
C(6)	0.1781 (10)	0.784 (1)	0.4416 (5)	8. (1)	7. (1)	1.6 (2)	−0.2 (9)	−0.3 (4)	−1.0 (4)
O(6)	0.1448 (8)	0.8535 (6)	0.4238 (3)	14.9 (10)	5.1 (6)	2.4 (2)	1.8 (7)	−0.8 (4)	0.1 (3)
C(7)	0.1258 (10)	0.6635 (9)	0.5214 (5)	7.0 (9)	7.5 (9)	1.6 (2)	1.2 (9)	0.1 (4)	−0.8 (4)
O(7)	0.0656 (7)	0.6662 (8)	0.5508 (3)	8.9 (7)	14.2 (10)	1.9 (2)	2.6 (8)	1.3 (3)	−0.5 (4)
C(8)	0.2214 (7)	0.4436 (7)	0.4254 (3)	3.8 (6)	4.1 (6)	1.0 (2)	−0.9 (6)	−0.2 (3)	0.3 (3)
C(9)	0.1085 (7)	0.3172 (7)	0.3352 (4)	3.0 (6)	4.9 (7)	1.3 (2)	−0.1 (6)	0.1 (3)	−0.1 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(7)	0.200	0.375	0.430	4.0	H(9)	0.080	0.277	0.305	4.0
H(8)	0.091	0.281	0.368	4.0					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^3.

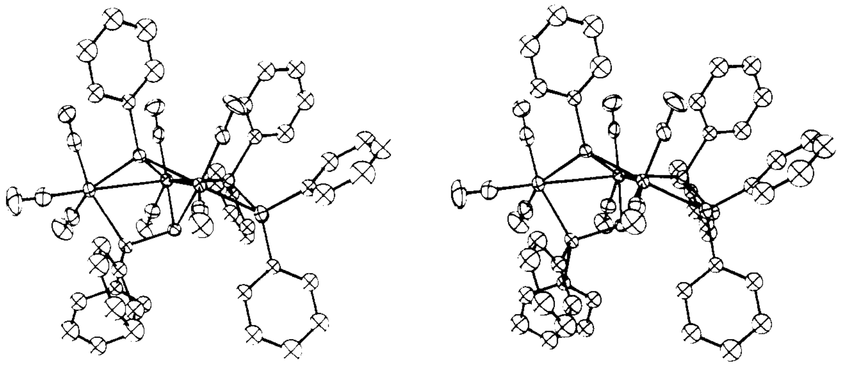

Figure 2. ORTEP stereoscopic view of the complex $Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$.

Table III. Selected Interatomic Distances (Å)

Ru(1)-Ru(2)	2.843 (1)	P(1)-C(10)	1.838 (7)
Ru(2)-Ru(3)	2.884 (1)	P(2)-C(8)	1.768 (9)
Ru(1)···Ru(3)	4.081 (1)	P(3)-C(9)	1.84 (1)
Ru(1)-C(1)	1.85 (1)	P(4)-C(9)	1.84 (1)
Ru(1)-C(2)	1.91 (1)	C(1)-O(1)	1.16 (1)
Ru(2)-C(3)	1.89 (1)	C(2)-O(2)	1.14 (1)
Ru(2)-C(4)	1.90 (1)	C(3)-O(3)	1.17 (1)
Ru(3)-C(5)	1.92 (1)	C(4)-O(4)	1.15 (1)
Ru(3)-C(6)	1.89 (1)	C(5)-O(5)	1.13 (1)
Ru(3)-C(7)	1.94 (1)	C(6)-O(6)	1.16 (1)
Ru(1)-C(8)	2.128 (9)	C(7)-O(7)	1.13 (1)
Ru(2)-C(8)	2.173 (9)	P(2)-C(16)	1.836 (7)
Ru(1)-P(1)	2.292 (3)	P(2)-C(22)	1.829 (7)
Ru(2)-P(1)	2.394 (3)	P(3)-C(28)	1.827 (7)
Ru(3)-P(1)	2.336 (3)	P(3)-C(34)	1.831 (7)
Ru(3)-P(2)	2.360 (3)	P(4)-C(40)	1.837 (6)
Ru(1)-P(3)	2.325 (3)	P(4)-C(46)	1.846 (6)
Ru(2)-P(4)	2.317 (3)		

were refined as rigid groups (D_{6h} symmetry; C–C 1.392 Å; C–H 0.95 Å). The final agreement factors were $R_w = 0.038$ and $R = 0.035$. The three largest peaks on a final difference Fourier synthesis were of height 0.56–0.80 e/Å^3 and were close to the C–C bonds of the benzene rings.

Atomic coordinates and anisotropic thermal parameters are listed in Table II; selected interatomic distances and bond angles are presented in Table III and IV.

Results and Discussion

Complex **2** can be formulated as $Ru_3(CO)_7(\mu_3\text{-}P(C_6H_5))(\mu\text{-}CHP(C_6H_5)_2)(dppm)$ on the basis of the X-ray structure, thus revealing the oxidative cleavage of a coordinated dppm ligand.

The asymmetric unit (Figure 1 and 2) consists of a triangular array of metal atoms involving two metal–metal distances closely related to $Ru_3(CO)_{12}$ [Ru(1)–Ru(2) 2.843 (1) Å, Ru(2)–Ru(3) 2.884 (1) Å] the third one being clearly nonbonding [Ru(1)···Ru(3) 4.081 (1) Å). A dppm ligand is still bridging the metal–metal bond, Ru(1)–Ru(2) as referred to the parent complex of **1**, $Ru_3(CO)_8(dppm)_2$. The metal framework is supported by two face-bridging organic moieties.

(i) The first is the fragment $\mu\text{-}CHP(C_6H_5)_2$ which functions as a tridentate ligand through the bridging carbon atom C(8) [Ru(1)–C(8) 2.128 (9) Å, Ru(2)–C(8) 2.173 (9) Å] and the phosphorus atom P(2) [Ru(3)–P(2) 2.360 (3) Å]. [Let us mention a significant shortening of the bond P(2)–C(8) 1.768 (9) Å relative to the mean value of 1.84 Å of P–C bonds in

Table IV. Selected Bond Angles (Deg)

Ru(1)–Ru(2)–Ru(3)	90.91 (3)	C(5)–Ru(3)–C(6)	96.7 (5)
Ru(2)–Ru(1)–Ru(3)	44.95 (3)	C(6)–Ru(3)–Ru(2)	92.8 (4)
Ru(2)–Ru(3)–Ru(1)	44.14 (3)	Ru(2)–Ru(3)–P(2)	71.95 (7)
C(1)–Ru(1)–C(8)	103.9 (4)	P(2)–Ru(3)–C(5)	97.4 (4)
C(8)–Ru(1)–Ru(2)	49.3 (3)	C(5)–Ru(3)–P(1)	109.5 (4)
Ru(2)–Ru(1)–C(2)	117.9 (3)	C(6)–Ru(3)–P(1)	88.2 (4)
C(2)–Ru(1)–C(1)	88.8 (5)	Ru(2)–Ru(3)–P(1)	53.34 (7)
C(1)–Ru(1)–P(1)	112.3 (4)	P(2)–Ru(3)–P(1)	81.57 (9)
C(8)–Ru(1)–P(1)	79.6 (3)	C(5)–Ru(3)–C(7)	99.9 (5)
Ru(2)–Ru(1)–P(1)	54.30 (7)	C(6)–Ru(3)–C(7)	91.1 (5)
C(2)–Ru(1)–P(1)	93.7 (3)	Ru(2)–Ru(3)–C(7)	97.3 (3)
C(1)–Ru(1)–P(3)	94.5 (4)	P(2)–Ru(3)–C(7)	92.3 (4)
C(8)–Ru(1)–P(3)	85.3 (3)	Ru(1)–P(1)–Ru(2)	74.67 (9)
Ru(2)–Ru(1)–P(3)	97.79 (7)	Ru(2)–P(1)–Ru(3)	75.14 (9)
C(2)–Ru(1)–P(3)	96.0 (3)	Ru(1)–P(1)–Ru(3)	123.7 (1)
C(3)–Ru(2)–C(4)	96.1 (5)	Ru(1)–P(1)–C(10)	120.2 (2)
C(4)–Ru(2)–C(8)	93.4 (4)	Ru(2)–P(1)–C(10)	128.0 (3)
C(8)–Ru(2)–Ru(1)	47.9 (2)	Ru(3)–P(1)–C(10)	115.8 (2)
Ru(1)–Ru(2)–C(3)	123.1 (3)	Ru(1)–C(1)–O(1)	177.5 (6)
C(3)–Ru(2)–Ru(3)	97.0 (3)	Ru(1)–C(2)–O(2)	176.4 (6)
C(4)–Ru(2)–Ru(3)	87.1 (3)	Ru(2)–C(3)–O(3)	177.2 (6)
C(8)–Ru(2)–Ru(3)	78.3 (2)	Ru(2)–C(4)–O(4)	177.0 (6)
C(3)–Ru(2)–P(1)	92.9 (3)	Ru(3)–C(5)–O(5)	177.7 (8)
C(4)–Ru(2)–P(1)	138.4 (3)	Ru(3)–C(6)–O(6)	175.9 (7)
C(8)–Ru(2)–P(1)	76.5 (2)	Ru(3)–C(7)–O(6)	176.6 (7)
Ru(1)–Ru(2)–P(1)	51.04 (7)		
C(3)–Ru(2)–P(4)	91.4 (3)		
C(4)–Ru(2)–P(4)	92.8 (3)		
C(8)–Ru(2)–P(4)	93.3 (2)		
Ru(1)–Ru(2)–P(4)	83.84 (7)		

this structure; this would suggest a bond order slightly higher than 1. The closely related organic fragment $CHP(Me)_2$ was previously derived[9] from the pyrolysis of $Os_3(CO)_{11}(PMe_3)_2$.]

(ii) The second is a phosphinidene ligand μ_3-$P(C_6H_5)$ linked to the three metal atoms in slightly asymmetric fashion [Ru(1)–P(1) 2.292 (3) Å, Ru(2)–P(1) 2.394 (3) Å Ru(3)–P(1) 2.336 (3) Å]. A salient feature is the distorted tetrahedral geometry of the phosphorus atom P(1), since this atom is only 0.05 Å out of the plane Ru(1)–Ru(3)–C(10). This distorsion has already been observed[10–12] and is sometimes assigned to a particular bonding sheme.[10] However, the observed geometry could be related to steric requirements about the open cluster.

The formation of this species from the parent complex **1** can be related to the known ability of transition-metal clusters to cleave P–C or As–C bonds,[12–17] sometimes leading to a naked phosphorus atom.[18] To our knowledge, the phosphinidene ligand has been rarely stabilized through a simple pyrolytic reaction[12,17] but through a different preparative route.[19–27]

At the present time, the precise nature of the mechanistic details of this oxidative addition remains uncertain. The first step of such a reaction could be the metalation of a CH bond;[28,29] as pointed out earlier,[30] the oxidative addition of a CH bond could be favored by a high electron density at the metal centers, which is precisely the case in the complex $Ru_3(CO)_8(dppm)_2$. A prerequisite for metalation is to bring a CH bond in close proximity to a metal center. In the present case, this could be achieved by rotation of a Ru–P bond from the equatorial plane to an axial position. Molecular models show that such a move brings a benzene ring close to a ruthenium center, thus favoring metalation. This is in agreement with the fact that the tripod ligand $((C_6H_5)_2P)_3CH$ does not undergo oxidative addition with $Ru_3(CO)_{12}$:[4] indeed, the rigid face-capped position of a tripod prevents any interaction between benzene rings and metal centers.

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Registry No. **1**, 77611-27-9; **2**, 77611-28-0; $Ru_3(CO)_{12}$, 15243-33-1.

Supplementary Material Available: Listings of rigid-group positional and thermal parameters and of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Binuclear Chloro Complexes of Tantalum(III) with Tantalum–Tantalum Double Bonds

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In the course of studying lower valent molecular compounds of the group 5 elements niobium and tantalum, we have investigated the structures of two binuclear tantalum compounds containing double bonds between the metal atoms. One of these is a compound first reported by McCarley and coworkers,[1] $Ta_2Cl_6(THT)_3$ (**1**), where THT = tetrahydrothiophene. As expected this compound forms crystals that are isotypic to those of $Ta_2Br_6(THT)_3$, the structure of which was recently reported by McCarley.[2] The reason for carrying out the structure analysis was to see how much the change from μ-Br ligands to μ-Cl ligands would affect the length of the Ta=Ta bond. We have also investigated the structure of the analogous compound $Ta_2Cl_6(Me_2S)_3$ (**2**). This is a new compound, although its niobium analogue has been reported before.[3] In this paper we report in detail these two structures

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