Related $(R_3E)_2V(CO)_5^-$, where $R_3E = (C_6H_{11})_3Sn$ and Ph_3Pb, are similarly prepared in moderate (40–70%) yields by treatment of **1** with 2 equiv of the corresponding R_3EX. Although analogous $R_3EV(CO)_5^{2-}$ have not been isolated from the reaction of 1 equiv of R_3EX with **1**, it is very likely that these are intermediates in the process

$$V(CO)_5^{3-} \xrightarrow[-X^-]{R_3EX} [R_3EV(CO)_5]^{2-} \xrightarrow[-X^-]{R_3EX} [(R_3E)_2V(CO)_5]^{1-}$$

Infrared spectra of these bis adducts are very similar to that of $(Ph_3Sn)_2V(CO)_5^-$ which strongly suggests that they also contain seven-coordinate vanadium. These materials are closely related to previously reported neutral $(R_3P)(R_3Sn)V(CO)_5$ which were assumed but not proven to contain seven-coordinate vanadium. On the basis of our results there is no reason to doubt this assumption.[18]

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Highly Reduced Organometallics. 5.[1] Synthesis, Properties, and the Molecular Structure of $(Ph_3PAu)_3V(CO)_5$, A Gold–Vanadium Cluster

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Abstract: The unusual metal cluster tris((triphenylphosphine)gold)pentacarbonylvanadium, $(Ph_3PAu)_3V(CO)_5$ (**1**), has been synthesized by treatment of sodium or cesium salts of the pentacarbonylvanadate(3–) ion, $V(CO)_5^{3-}$, with chloro(triphenylphosphine)gold in liquid ammonia (10–15% yields) or in tetrahydrofuran (50–60% yields). An X-ray crystallographic structure determination of this substance shows that **1** is the first neutral derivative of the unknown tetrahedral cluster $(Ph_3PAu)_4$ as well as the only established mixed-metal cluster containing vanadium. In **1** eight-coordinate vanadium is bound to a novel tridentate tris(triphenylphosphine)trigold ligand containing gold–gold bonds. All four metal atoms form a slightly distorted tetrahedral cluster. The $V(CO)_5$ group in **1** is best described as being a pseudooctahedral fragment which is bound to a large trigold unit. Infrared spectra of **1** support this view as they resemble those of the octahedral anions $V(CO)_5L^-$, where L = PR_3, CNR, etc. Chemical reactivity studies demonstrate that **1** is a remarkably robust gold–vanadium carbonyl complex. Triphenylphosphine, soluble halide, and acetonitrile which normally cause facile heterolytic cleavage of gold–vanadium bonds at room temperature are found to have no effect on **1**. Crystal data: space group $P\bar{1}$, $a = 12.840\ (6)$ Å, $b = 19.088\ (6)$ Å, $c = 12.380\ (4)$ Å, $\alpha = 93.82\ (3)°$, $\beta = 117.26\ (3)°$, $\gamma = 92.02\ (3)°$, $Z = 2$, $V = 2684\ (4)$ Å^3, and ρ(calcd) = 1.941 g/cm^3.

Mixed-metal clusters have attracted wide attention in recent years due to their possible use as homogeneous catalysts and precursors to well-defined bimetallic or multimetallic heterogeneous catalysts.[2] Although metal clusters containing only gold atoms are now very numerous and have been shown to adopt a variety of unusual geometries,[3] only three compounds likely, but not confirmed, to contain mixed-metal clusters of gold and other transition metals have been previously reported. These are $Os_3(CO)_{10}(Ph_3PAu)X$ (X = H,[4] halide[5]) and $Os_3(CO)_{10}S_2(AuPPh_3)_2$.[5] Except for an unusual ferrocene derivative, $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2(PPh_3)_2]^+$, which has been shown to contain an open Fe–Au–Au metal chain and a formally four-coordinate central gold atom,[6] all other mixed gold–transition-metal compounds have been proposed to contain two-coordinate gold. These include AuX_2^- (where X = $CpMo(CO)_3$, $Mn(CO)_5$, $CpFe(CO)_2$, $Co(CO)_4$),[7] $(Ph_3PAu)_2M(CO)_4$ (M = Fe,[8] Ru,[9] Os[10]), and $(Ph_3PAu)_3M'(CO)_4$ (M' = Mn, Re).[11] In a preliminary report, we implied that $(Ph_3PAu)_3V(CO)_5$ also contained normal two-coordinate gold bound to an unprecedented eight-coordinate vanadium.[12] However, since alternative formulations involving lower coordination numbers for the vanadium (e.g., $(Ph_3PAu)_2V(CO)_4(CO \rightarrow AuPPh_3)$) could not be ruled out and also because this substance was much less reactive and more thermally stable than previously prepared compounds containing gold–vanadium bonds, the molecular structure of $(Ph_3PAu)_3V(CO)_5$ was determined by single-crystal X-ray diffraction techniques. In this paper we present the results of this study and discuss in detail the synthesis and chemical and physical properties of this interesting molecule.

Experimental Section

For general procedures, solvent purification and the synthesis of $Na_3V(CO)_5$ and $Cs_3V(CO)_5$ refer to the previous paper in this series.[1] Chloro(triphenylphosphine)gold was prepared according to a published procedure.[13]

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Table I. Summary of Crystal Data and Intensity Collection for $(Ph_3PAu)_3V(CO)_5$

(A) Crystal Parameters at 23 °C

space group: $P\bar{1}$
$a = 12.840$ (6) Å
$b = 19.088$ (6) Å
$c = 12.380$ (4) Å
$\alpha = 93.82$ (3)°
$\beta = 117.26$ (3)°
$\gamma = 92.02$ (3)°

$V = 2684$ (4) Å
$Z = 2$
mol wt 1568.78
ρ(calcd) = 1.941 g/cm³
cryst dimens: 0.13 × 0.26 × 0.36 mm

(B) Measurement of Intensity Data

radiation: λ(Mo Kα) = 0.710 73 Å
monochromator: graphite
abs coeff = 87.633 cm⁻¹
2θ limits = 0–48
final number of variables: 371
unique data used: 6490, $F_o^2 \geqslant 3.0\sigma(F_o^2)$
$R^a = 0.030$
$R_w{}^a = 0.036$
error in observn of unit wt: 1.49

[a] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, $R = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o|)$, and $R_w = (\Sigma w(|F_o| - |F_c|))^2/(\Sigma w(|F_o| - |F_c|))^2/(\Sigma w |F_o|^2]^{1/2}$.

Synthesis of Tris((triphenylphosphine)gold)pentacarbonylvanadium(0), $(Ph_3PAu)_3V(CO)_5$ (1). Method A. To a vessel containing solid $Cs_3V(CO)_5$ (0.837 g, 1.42 mmol) and Ph_3PAuCl (2.106 g, 4.26 mmol) was added THF (70 mL) with stirring at room temperature. Within 15 s the solution became red. After 1 h the deep red solution was filtered (medium porosity frit) and THF was removed slowly until crystal formation commenced. (Formation of crystals should occur before the next step is attempted, otherwise an intractable oil often results). Then diethyl ether (100 mL) was added dropwise to the solution which caused extensive crystal formation. The brownish supernatant containing other, as yet uncharacterized, gold–vanadium species was removed. The remaining red crystalline product was washed with ether (3 × 10 mL) until the washings were nearly colorless. An additional recrystallization from THF–diethyl ether provided analytically pure **1** in reasonable yield (1.44 g, 60%). Anal. Calcd for $C_{59}H_{45}O_5Au_3P_3V$: C, 45.17; H, 2.89; P, 5.92; mol wt 1569. Found: C, 45.62; H, 3.06; P, 6.10; mol wt in THF 1570 (mp 139–140 °C). Compound **1** consists of air-stable dark red crystals which dissolve to provide only slightly air-sensitive solutions in a variety of organic solvents including benzene, THF, methylene chloride, and acetone. Compound **1** is slightly soluble in acetonitrile and insoluble in diethyl ether, alkanes, neat HMPA, nitromethane, and water. For infrared spectra of **1**, see Results and Discussion.

Method B. Much lower yields of the identical product **1** can be prepared by treatment of $Na_3V(CO)_5$ in liquid ammonia with 3 equiv of Ph_3PAuCl. For example, from the reactant quantities (1.30 g of $[Na(diglyme)_2][V(CO)_6]$, 0.19 g of Na metal in 50 mL of NH_3, 3.69 g of Ph_3PAuCl), there was obtained after a THF–heptane recrystallization 0.45 g (12% yield) of purple crystalline solid which was spectrally and analytically identical with **1**. Anal. Found: C, 44.94; H, 2.92; P, 5.60.

Crystal Preparation and Crystallographic Analysis of $(Ph_3PAu)_3V(CO)_5$. Ether (5 mL) was layered on and allowed to slowly diffuse through a deep red tetrahydrofuran solution (10 mL) containing 0.16 g of **1**. After 3 days well-formed air-stable deep red crystals had formed. These were washed with ether (3 × 20 mL) and isobutane (2 × 20 mL) and dried in vacuo. A square-based pyramidal crystal was cut from a larger cluster and used in the structure determination. The crystal belonged to the triclinic crystal class by the Enraf-Nonius CAD 4-SDP peak search and centering and indexing programs and by a Dulaney reduction calculation.[14] The space group $P\bar{1}$ was verified by successful solution and refinement. Data collections were carried out on a CAD 4 Nonius diffractometer. Background counts were measured at both ends of the scan range with the use of an ω–2θ scan equal to half the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and no decay with time was observed. The intensities of 8396 ($+h$, $\pm k$, $\pm l$) unique reflections were measured at 23 °C out to 2θ of 48° for **1**. The data were corrected for Lorentz, polarization, absorption (maximum and minimum transmission coefficients were 76.18 and 99.95), and background effects, using a value of 0.03 for p.[15] Of the 8396 unique reflections for **1**, 65% have $F_o^2 \geq 3.0\sigma(F_o^2)$ and were used in subsequent calculations. A summary of crystal data and intensity collection for **1** is presented in Table I.

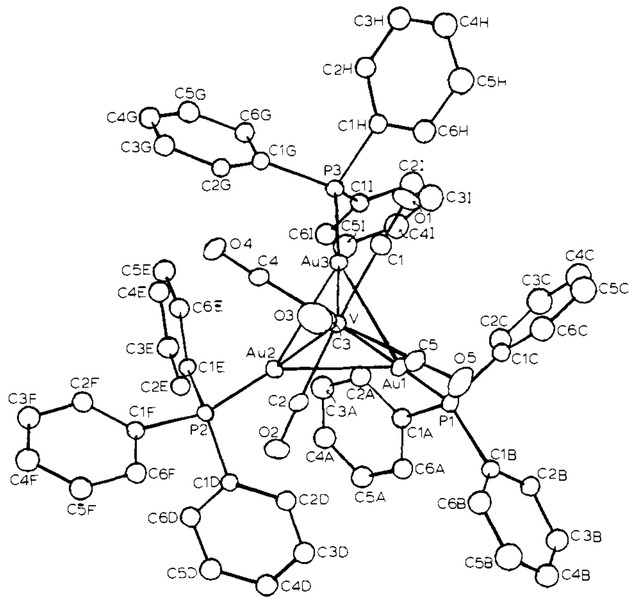

Figure 1. View of the molecular structure of $(Ph_3PAu)_3V(CO)_5$ showing the labeling scheme and the orientation of the phenyl rings.

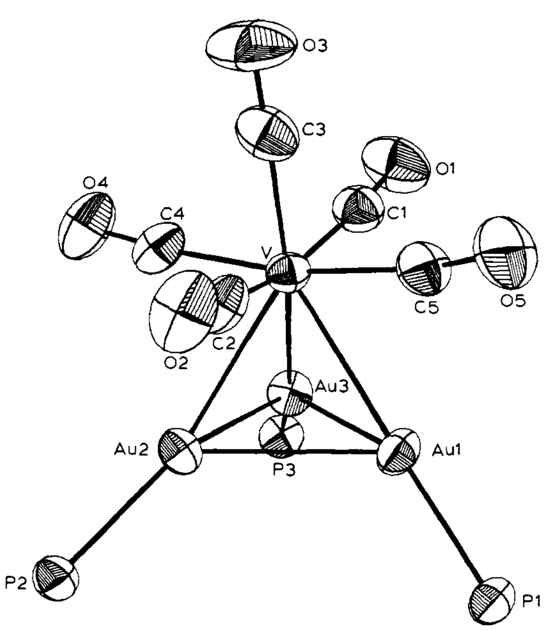

Figure 2. ORTEP drawing of $(Ph_3PAu)_3V(CO)_5$. The phenyl carbon atoms have been omitted for clarity, and the ellipsoids are drawn with 30% probability boundaries.

Solution and Refinement of the Structure for 1. Conventional heavy-atom techniques were used in solving the structure of **1**. The Au atoms were located by Patterson synthesis. Full-matrix least-squares refinement and difference Fourier calculations were used to locate all remaining nonhydrogen atoms.[16] The atomic scattering factors were taken from

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(14) All calculations were carried out on PDP 8A and 11/34 computers by using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. Also: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978.

(15) The intensity data were processed as described: "CAD 4 and SDP Users Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/\mathrm{NPI})(C - 2B)$, where $K = 20.1166\times$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Au(1)	0.08659 (2)	0.31131 (2)	0.22752 (2)	0.00610 (2)	0.00168 (1)	0.00679 (2)	−0.00071 (2)	0.00613 (3)	−0.00087 (2)
Au(2)	0.11990 (2)	0.16581 (2)	0.23939 (2)	0.00565 (2)	0.00200 (1)	0.00609 (2)	0.00132 (2)	0.00401 (3)	0.00181 (2)
Au(3)	0.06857 (2)	0.23266 (2)	0.02279 (2)	0.00606 (2)	0.00217 (1)	0.00579 (2)	0.00050 (2)	0.00732 (2)	0.00068 (2)
V	−0.09582 (9)	0.21122 (6)	0.10453 (9)	0.00438 (7)	0.00192 (3)	0.00545 (8)	0.00007 (9)	0.0049 (1)	0.00033 (9)
P(1)	0.2386 (2)	0.3960 (1)	0.3328 (2)	0.0063 (1)	0.00189 (6)	0.0072 (1)	−0.0007 (1)	0.0062 (2)	−0.0004 (2)
P(2)	0.2735 (2)	0.1031 (1)	0.3593 (2)	0.0054 (1)	0.00207 (5)	0.0056 (1)	0.0007 (1)	0.0039 (2)	0.0015 (1)
P(3)	0.1527 (2)	0.2352 (1)	−0.1058 (2)	0.0060 (1)	0.00229 (6)	0.0061 (1)	0.0001 (1)	0.0070 (2)	0.0005 (1)
O(1)	−0.2163 (5)	0.2706 (3)	−0.1500 (5)	0.0090 (5)	0.0051 (2)	0.0086 (4)	0.0029 (6)	0.0061 (7)	0.0062 (5)
O(2)	−0.0673 (5)	0.1505 (3)	0.3424 (4)	0.0168 (5)	0.0037 (2)	0.0086 (4)	−0.0010 (6)	0.0159 (6)	0.0017 (5)
O(3)	−0.3452 (5)	0.1545 (4)	0.0418 (6)	0.0067 (4)	0.0071 (3)	0.0168 (6)	−0.0034 (6)	0.0110 (7)	0.0044 (7)
O(4)	−0.1011 (5)	0.0666 (3)	−0.0327 (5)	0.0139 (5)	0.0027 (2)	0.0101 (5)	−0.0026 (5)	0.0125 (7)	−0.0030 (5)
O(5)	−0.1649 (5)	0.3471 (4)	0.1972 (6)	0.0119 (5)	0.0043 (2)	0.0178 (6)	0.0044 (5)	0.0152 (8)	−0.0044 (6)
C(1)	−0.1647 (6)	0.2504 (4)	−0.0559 (6)	0.0061 (5)	0.0027 (2)	0.0081 (6)	0.0004 (6)	0.0070 (8)	0.0015 (6)
C(2)	−0.0686 (6)	0.1734 (4)	0.2571 (6)	0.0094 (6)	0.0021 (2)	0.0063 (5)	−0.0010 (6)	0.0084 (8)	−0.0012 (6)
C(3)	−0.2507 (6)	0.1770 (5)	0.0644 (7)	0.0073 (5)	0.0039 (3)	0.0087 (6)	0.0022 (7)	0.0085 (8)	0.0026 (7)
C(4)	−0.0927 (6)	0.1202 (4)	0.0203 (6)	0.0080 (5)	0.0024 (2)	0.0061 (5)	−0.0018 (6)	0.0067 (8)	−0.0001 (6)
C(5)	−0.1302 (6)	0.2985 (4)	0.1665 (6)	0.0069 (5)	0.0030 (3)	0.0091 (6)	0.0016 (6)	0.0099 (7)	−0.0008 (7)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
C1A	0.3790 (6)	0.3569 (4)	0.3958 (6)	3.8 (2)	C4A	0.5849 (8)	0.2874 (5)	0.4840 (8)	5.5 (2)
C1B	0.2392 (6)	0.4479 (4)	0.4611 (6)	3.3 (1)	C4B	0.2407 (8)	0.5209 (5)	0.6671 (8)	5.5 (2)
C1C	0.2521 (6)	0.4610 (4)	0.2373 (6)	3.4 (2)	C4C	0.2632 (9)	0.5601 (6)	0.0868 (9)	7.1 (3)
C1D	0.3601 (6)	0.1443 (4)	0.5146 (6)	3.0 (1)	C4D	0.4894 (7)	0.2096 (5)	0.7508 (7)	4.8 (2)
C1E	0.3729 (6)	0.0884 (4)	0.2936 (6)	2.9 (1)	C4E	0.5090 (7)	0.0634 (5)	0.1736 (7)	4.7 (2)
C1F	0.2297 (6)	0.0156 (4)	0.3816 (6)	3.1 (1)	C4F	0.1546 (7)	0.8842 (8)	0.4188 (8)	5.1 (2)
C1G	0.1747 (6)	0.1466 (4)	−0.1533 (6)	3.1 (1)	C4G	0.1968 (7)	0.0108 (5)	−0.2303 (7)	4.3 (2)
C1H	0.0610 (6)	0.2727 (4)	−0.2476 (6)	3.4 (2)	C4H	−0.0802 (8)	0.3303 (6)	−0.4613 (9)	6.1 (2)
C1I	0.2939 (6)	0.2848 (4)	−0.0520 (6)	3.4 (2)	C4I	0.5087 (9)	0.3617 (6)	0.0345 (9)	6.7 (3)
C2A	0.3951 (7)	0.3062 (5)	0.3175 (7)	4.5 (2)	C5A	0.5702 (8)	0.3350 (8)	0.5620 (8)	5.3 (2)
C2B	0.3104 (6)	0.5098 (4)	0.5141 (7)	4.0 (2)	C5B	0.1660 (9)	0.4607 (6)	0.6090 (10)	7.3 (3)
C2C	0.3598 (8)	0.4768 (5)	0.2355 (8)	5.3 (2)	C5C	0.1605 (9)	0.5482 (6)	0.0922 (9)	7.1 (3)
C2D	0.3359 (6)	0.2118 (4)	0.5441 (7)	3.9 (2)	C5D	0.5123 (7)	0.1422 (5)	0.7249 (7)	4.9 (2)
C2E	0.4943 (6)	0.0937 (4)	0.3600 (7)	3.8 (2)	C5E	0.3858 (7)	0.0567 (5)	0.1067 (8)	5.1 (2)
C2F	0.2572 (7)	−0.0468 (4)	0.3354 (7)	4.1 (2)	C5F	0.1241 (7)	−0.0550 (5)	0.4631 (7)	4.8 (2)
C2G	0.1032 (6)	0.0909 (4)	−0.1507 (6)	3.3 (1)	C5G	0.2689 (7)	0.0652 (5)	−0.2323 (7)	4.7 (2)
C2H	0.0720 (7)	0.2568 (5)	−0.3552 (7)	4.3 (2)	C5H	−0.0965 (9)	0.3490 (6)	−0.3576 (9)	6.7 (3)
C2I	0.2992 (8)	0.3504 (6)	−0.0901 (8)	6.1 (2)	C5I	0.5070 (8)	0.2966 (6)	0.0757 (9)	6.1 (2)
C3A	0.5006 (8)	0.2723 (5)	0.3630 (8)	5.8 (2)	C6A	0.4640 (7)	0.3712 (5)	0.5183 (7)	4.5 (2)
C3B	0.3099 (8)	0.5448 (5)	0.6185 (8)	5.2 (2)	C6B	0.1646 (8)	0.4240 (5)	0.5052 (8)	5.4 (2)
C3C	0.3613 (9)	0.5272 (6)	0.1582 (9)	7.1 (3)	C6C	0.1518 (8)	0.4954 (6)	0.1678 (9)	6.2 (2)
C3D	0.4019 (7)	0.2440 (5)	0.6629 (7)	4.7 (2)	C6D	0.4473 (6)	0.1079 (4)	0.6043 (7)	4.0 (2)
C3E	0.5617 (7)	0.0819 (5)	0.2973 (7)	4.9 (2)	C6E	0.3184 (6)	0.0701 (4)	0.1665 (7)	4.0 (2)
C3F	0.2202 (7)	−0.1117 (5)	0.3562 (7)	4.7 (2)	C6F	0.1609 (7)	0.0119 (4)	0.4438 (7)	4.1 (2)
C3G	0.1134 (7)	0.2636 (4)	−0.1904 (7)	4.2 (2)	C6G	0.2573 (6)	0.1346 (4)	−0.1957 (7)	4.0 (2)
C3H	−0.0012 (7)	0.2861 (5)	−0.4631 (8)	5.1 (2)	C6H	−0.0212 (7)	0.3179 (5)	−0.2471 (8)	5.0 (2)
C3I	0.4120 (9)	0.3911 (6)	−0.0425 (10)	7.4 (3)	C6I	0.3953 (7)	0.2570 (5)	0.0304 (7)	4.9 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

the usual tabulation.[17] A table of observed and calculated structure factors for **1** is available.[18] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were not located in the final difference Fourier maps and therefore were not included, and no chemically significant peaks were observed in these maps. The final positional and thermal parameters of the atoms appear in Table II. A view of the molecular structure of **1** showing the labeling scheme and the orientation of the phenyl rings is shown in Figure 1. Figure 2 presents an ORTEP drawing of **1** where phenyl groups have been omitted for clarity, and the ellipsoids are drawn with 30% probability boundaries.

Results and Discussion

Synthesis of $(Ph_3PAu)_3V(CO)_5$ (1). Treatment of liquid ammonia solutions of $Na_3V(CO)_5$ or tetrahydrofuran slurries of $Cs_3V(CO)_5$ with 3 equiv of Ph_3PAuCl produces varying yields (10–15% from Na salt; 50–60% from cesium salt) of a novel neutral product whose spectral and analytical data are consistent with the formulation $(Ph_3PAu)_3V(CO)_5$. The poor yields of product obtained from the liquid ammonia reaction are likely due to ammonolysis of the Ph_3PAuCl since **1** is stable in liquid ammonia. In the synthesis of **1** from $Cs_3V(CO)_5$, we have demonstrated the importance of the availability of an ammonia-free source of $V(CO)_5{}^{3-}$. On the basis of our results with Ph_3PAuCl, it is clear that $Cs_3V(CO)_5$ as well as corresponding niobium and tantalum species should be valuable precursors to other compounds containing metal–metal bonds.

Crystal Structure of 1. The crystal structure of **1** demonstrates that eight-coordinate vanadium is indeed present as we had previously suggested[12] but also shows more interesting features including the presence of a novel tetrahedral cluster containing three gold atoms and one vanadium atom and a new tridentate gold ligand containing gold–gold bonds, *tris(triphenylphosphine)trigold.* One can consider this species to be a derivative of the presently unknown tetrahedral cluster, $(Ph_3PAu)_4$, where the $V(CO)_5$ unit replaces one Ph_3PAu group, which contains gold in the 0 formal oxidation state. The reaction of $V(CO)_5{}^{3-}$ with Ph_3PAuCl is probably best thought of as a redox process where the "super-reduced" trianion formally converts Au(I) to Au(0). The tris(triphenylphosphine)trigold unit is electronically analogous to a coordinated cyclopropenyl group where both may be considered to be three-electron donors.[19] In this sense **1** resembles

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(16) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight is $[\sum w|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively.

(17) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV, Table 2.2.4. Cromer, D. T., *Ibid.* Table 2.3.1.

(18) See paragraph at end of paper regarding supplementary material.

(19) $(C_3Ph_3)V(CO)_5$ has been reported: Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 345.

Table III. Selected Distances and Angles with Esd's for $(Ph_3PAu)_3V(CO)_3$

a. Distances (Å)			
V-Au(1)	2.736 (1)	C(4)-O(4)	1.152 (8)
V-Au(2)	2.709 (1)	C(5)-O(5)	1.158 (8)
V-Au(3)	2.756 (1)	Au(1)-P(1)	2.300 (2)
Au(1)-Au(2)	2.828 (0)	Au(2)-P(2)	2.291 (2)
Au(1)-Au(3)	2.768 (0)	Au(3)-P(3)	2.299 (2)
Au(2)-Au(3)	2.855 (0)	P(1)-C(1A)	1.817 (7)
V-C(1)	1.980 (7)	P(1)-C(1B)	1.812 (7)
V-C(2)	1.951 (7)	P(1)-C(1C)	1.826 (7)
V-C(3)	1.894 (8)	P(2)-C(1D)	1.826 (6)
V-C(4)	1.978 (7)	P(2)-C(1E)	1.820 (6)
V-C(5)	1.936 (7)	P(2)-C(1F)	1.821 (6)
C(1)-O(1)	1.147 (8)	P(3)-C(1G)	1.826 (6)
C(2)-O(2)	1.164 (7)	P(3)-C(1H)	1.821 (7)
C(3)-O(3)	1.172 (8)	P(3)-C(1I)	1.821 (7)

b. Angles (Deg)			
Au(1)VAu(2)	62.59 (2)	Au(3)Au(2)P(2)	132.20 (4)
Au(1)VAu(3)	60.53 (2)	Au(1)Au(3)P(3)	137.67 (4)
Au(2)VAu(3)	62.97 (2)	Au(2)Au(3)P(3)	134.02 (4)
Au(2)Au(1)Au(3)	61.33 (1)	VC(1)O(1)	172.5 (6)
Au(3)Au(1)V	60.11 (2)	VC(2)O(2)	171.6 (6)
Au(2)Au(1)V	58.24 (2)	VC(3)O(3)	178.2 (7)
Au(1)Au(2)Au(3)	58.30 (1)	VC(4)O(4)	174.2 (6)
Au(1)Au(2)V	59.17 (2)	VC(5)O(5)	171.6 (6)
Au(3)Au(2)V	59.33 (2)	C(1)VC(2)	165.4 (3)
Au(1)Au(3)Au(2)	60.37 (1)	C(1)VC(3)	86.7 (3)
Au(1)Au(3)V	59.36 (2)	C(1)VC(4)	88.3 (3)
Au(2)Au(3)V	57.70 (2)	C(1)VC(5)	86.0 (3)
VAu(1)P(1)	179.11 (5)	C(2)VC(3)	79.8 (3)
VAu(2)P(2)	164.65 (5)	C(2)VC(4)	95.6 (3)
VAu(3)P(3)	160.62 (5)	C(2)VC(5)	87.7 (3)
Au(2)Au(1)P(1)	122.12 (5)	C(3)VC(4)	83.8 (3)
Au(3)Au(1)P(1)	120.78 (4)	C(3)VC(5)	86.8 (3)
Au(1)Au(2)P(2)	133.51 (4)	C(4)VC(5)	169.3 (3)

a substituted pseudooctahedral complex of the type $V(CO)_5L$ where L is a very large ligand. In fact, the infrared spectrum of $(Ph_3PAu)_3V(CO)_5$ is similar to those of $V(CO)_5L^-$ species where L = CNR, PR_3, etc. (vide infra).

Metal-Metal Interactions in $(Ph_3PAu)_3V(CO)_5$. The four metal atoms are arranged in a slightly distorted tetrahedral array with Au-Au-V, Au-Au-Au, and Au-V-Au angles close to the expected 60° (Table III). Observed metal-metal bond lengths in **1** are compatible with the presence of Au-Au and Au-V single bonds. Previously reported bond distances, which are considered to correspond roughly to Au-Au single bonds, vary considerably, especially in cluster systems. Ranges of values for such bonds in several compounds and metallic gold are as follows: $Au_8(PPh_3)_8^{2+}$ (2.826–2.960 Å).[20] $Au_{11}[P(p\text{-}FC_6H_4)_3]_7I_3$ (2.600–3.187 Å),[21] $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2(PPh_3)_2]^+$ (2.768 Å),[6] $Au_9[P(p\text{-}MeC_6H_4)_3]_8^{3+}$ (2.68–2.86 Å),[22] and Au metal (2.884 Å).[23] In **1** the Au-Au distances range from 2.768 to 2.855 Å. The Au-V bond lengths in **1** range from 2.709 to 2.756 Å and are only slightly shorter than the Au-Au bonds. These Au-V distances are significantly longer than gold-first-row transition-metal bond lengths reported for other carbonyl derivatives. For example, the Au-Mn bond in $Ph_3PAuMn(CO)_4[P(OPh)_3]$ (2.57 Å)[24] and the Au-Co bond in $Ph_3PAuCo(CO)_4$ (2.50 Å)[25] are substantially shorter. The rather long Au-V bonds in **1** probably result from the larger size and higher coordination number of vanadium compared to manganese and cobalt in the previously mentioned compounds; however, their longer length may also be necessary to stabilize the nearly tetrahedral unit. Preliminary data on the crystal structure determination of seven-coordinate $Ph_3PAuV(CO)_6$[13] indicate an Au-V bond distance of 2.68 Å; however, the accuracy of this value is unknown.[26] A very long Au-Fe bond (2.818 (9) Å) is present in $[(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4)Au_2(PPh_3)_2]^+$.[6]

Metal-Ligand Interactions and the Ligands. Each gold atom is bound to one triphenylphosphine ligand. The Au-P bond lengths range from 2.291 (2) to 2.300 (2) Å and are similar to those reported for other (triphenylphosphine)gold complexes including $Au(CN)PPh_3$ (2.27 (1) Å),[27] $(\pi\text{-}C_5H_5)W(CO)_3AuPPh_3$ (2.25 (1) Å),[28] and $Au_8(Ph_3P)_8^{2+}$ (2.29–2.33 Å).[20] The phosphorus atoms of the triphenylphosphine groups lie far out of the plane defined by the gold atoms and away from the $V(CO)_5$ unit. The latter has essentially the geometry of an octahedral fragment; however, the four "equatorial" carbonyl groups are pushed toward the "axial" carbonyl group (with all C(*i*)VC(3) angles being significantly less than 90°) and away from the $(Ph_3PAu)_3$ group (see Table III). Infrared evidence (vide infra) indicates the (triphenylphosphine)trigold unit is a rather strong donor and structural evidence suggests that the "axial" carbonyl group, which is approximately trans to the gold triangle, is especially involved in back-bonding with the vanadium. Thus, the V-C(3) distance (1.894 (8) Å) is significantly shorter than the "equatorial" V-C(*i*) distances (1.936 (7)–1.980 (7) Å) while the "axial" C(3)-O(3) distance (1.172 (8) Å) is significantly longer than three of the four "equatorial" C(*i*)-O(*i*) distances (1.147 (8)–1.164 (7) Å). These distances agree well with corresponding values reported for $V(CO)_6^-$ (V-C (1.931 (9) Å), C-O (1.146 (11) Å)),[29] $(\eta^3\text{-}3\text{-}CH_3C_3H_4)V(CO)_3(diars)$ (V-C (1.93 (2)–1.97 (2) Å), C-O (1.11 (3)–1.14 (3) Å)),[30] and other vanadium carbonyl structures.[31-37]

Chemical and Spectral Properties of $(Ph_3PAu)_3V(CO)_5$ (1). When **1** was first characterized by elemental composition and molecular weight data, it was formulated as containing three noninteracting (triphenylphosphine)gold groups bound to a $V(CO)_5$ unit. However, it quickly became apparent that there was something special about this molecule since it was far less reactive than the two previously reported (triphenylphosphine)gold derivatives of vanadium carbonyl, $Ph_3PAuV(CO)_6$ and $Ph_3PAuV(CO)_5PPh_3$.[13] Both of these rapidly undergo heterolytic cleavage in acetonitrile and hexamethylphosphoramide (HMPA) according to eq 1. Also, these substances rapidly react with triphenylphosphine and soluble halide to heterolytically cleave the Au-V bonds, i.e.

$$Ph_3PAuV(CO)_{6-n}(Ph_3P)_n\ (n = 0,\ 1) + xS\ (S = CH_3CN \text{ or } HMPA) \rightarrow Ph_3PAuS_x^+ + V(CO)_{6-n}(Ph_3P)_n^- \quad (1)$$

$$Ph_3PAuV(CO)_{6-n}(Ph_3P)_n\ (n = 0,\ 1) + yPh_3P \rightarrow (Ph_3P)_{y+1}Au^+V(CO)_{6-n}(Ph_3P)_n^-$$

$$Ph_3PAuV(CO)_{6-n}(Ph_3P)_n\ (n = 0,\ 1) + Br^- \rightarrow Ph_3PAuBr + V(CO)_{6-n}(Ph_3P)_n^-$$

By contrast, we have no evidence that $(Ph_3PAu)_3V(CO)_5$ undergoes any substantial change in polar solvents at room temperature. The molecular weight of **1** in THF is consistent with the presence of $(Ph_3PAu)_3V(CO)_5$ in solution. Also, a 2.14×10^{-3} M solution of **1** in THF showed no conductivity. (It was insoluble in nitromethane.) Infrared spectra in the ν_{CO} region of

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$(Ph_3PAu)_3V(CO)_5$ are essentially identical in band number, position, and relative intensities in a variety of solvents (ν_{CO} of **1** in THF 1958 (vs), 1890 (w), 1834 (s); in CH_2Cl_2 1954 (vs), 1879 (sh), 1825 (s) cm^{-1}) including CH_2Cl_2, THF, CH_3CN, and HMPA-CH_2Cl_2 (50:50 v/v; (1) is insoluble in neat HMPA). Nujol mull spectra of crystalline **1** are very similar to solution spectra except the two bands at lower energy are split due to solid-state effects (ν_{CO} in Nujol 1959 (s), 1889 (m), 1876 (sh), 1828 (s), 1810 (s) cm^{-1}). As was mentioned earlier, the solution spectra of **1** resemble those of $V(CO)_5L^-$ species (e.g., ν_{CO} of $[Et_4N][V(CO)_5Ph_3P]$ in THF 1965 (s), 1858 (m), 1823 (vs).[38,39] It is evident from a comparison of these spectra that the $(Ph_3PAu)_3$ ligand is a strong donor group to vanadium. By contrast, all of the ν_{CO} values for $(Ph_3Sn)_2V(CO)_5^-$ in a variety of solvents are above 1860 cm^{-1}.[1] An analysis of the ν_{CO} values for $Ph_3PAuMn(CO)_5$ indicates that an individual Ph_3PAu unit acts as a fairly good π acceptor and a strong σ donor to manganese.[40]

Treatment of $(Ph_3PAu)_3V(CO)_5$ with 4 equiv of Ph_3P in THF or 10 equiv of $[Et_4N]Br$ in CH_2Cl_2 (all at room temperature) also gave no reaction after ca. 24 h. On the basis of the crystal structure of **1** which shows the presence of Au–Au bonds as well as Au–V bonds, it is not surprising that individual Ph_3PAu units cannot be readily displaced as they can in mono((triphenylphosphine)gold) complexes. Structures of bis- and other tris((triphenylphosphine)gold) derivatives of metal carbonyls (e.g., $(Ph_3PAu)_2M(CO)_4$ (M = Fe,[8] Ru,[9] Os[10]) and $(Ph_3PAu)_3M(CO)_4$ (M = Mn, Re))[11] have not been determined. It seems possible in view of our results that gold–gold interactions may also be present, especially in the seven-coordinate $(Ph_3PAu)_3M(CO)_4$ complexes.

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Supplementary Material Available: Tables of root-mean-square amplitudes of thermal vibration (Å) and final thermal parameters and structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.

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[39] However, it is important to note that the intensity patterns of the infrared active ν_{CO} bands of $(Ph_3PAu)_3V(CO)_5$ are much different than those of bonafide C_4V $M(CO)_5L$ species where the high frequency band ($A_1{}^2$ mode) is always weaker in intensity than the lower frequency band of E symmetry: cf. Dobson, G.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Chem. Nucl. Chem.* **1966**, *8*, 1.

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[41] **Note Added in Proof**: The molecular structure of $[(Ph_3PAu)_3Mn(CO)_4]$ has been determined and shows gold–gold interactions to be present (Ellis, J.; Warnock G., to be submitted). Also, a recent communication on the molecular structure of $[Au_4(\mu\text{-}I)_2(PPh_3)_4]$ shows this species to be a tetranuclear gold cluster and a derivative of $(Ph_3PAu)_4$ (De Martin, F.; Monassero, M.; Naldini, L.; Ruggeri, R.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1981**, 222).

Evidence for the Localized Fe(III)/Fe(II) Oxidation State Configuration as an Intrinsic Property of $[Fe_2S_2(SR)_4]^{3-}$ Clusters

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Abstract: Spectroscopic properties of the mixed-valence 2-Fe prosthetic group $[Fe_2S_2(S\text{–}Cys)_4]$ (**1**) of reduced ferredoxin proteins (Fd_{red}) have demonstrated the localized Fe(II) + Fe(III) (class II) oxidation state configuration. The lifetime of this configuration is $\gtrsim 10^{-7}$ s from spectra at 4.2–250 K and presumably at least $\sim 10^{-3}$ s at 300 K from ^1H NMR spectra. Reduction of the centrosymmetric Fd_{ox} analogue $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$ $S_{2\text{-}o\text{-}x}yl$ = *o*-xylene-α,α'-dithiolate) in solution by electrochemical or chemical means affords several products. One of these exhibits a nearly featureless UV/visible spectrum, a near-infrared absorption band at 1750 nm, a virtually axial EPR spectrum with $g = 2.01$ and 1.94 observable to at least 80 K, and a Mössbauer spectrum in zero field at 4.2–180 K containing features fully consistent with tetrahedral $Fe^{II}\,S_4$ ($\delta = 0.60$, $\Delta E_Q = 3.06$ mm/s) and $Fe^{III}S_4$ sites ($\delta = 0.19$, $\Delta E_Q = 0.54$ mm/s). These properties are very similar to those of Fd_{red} proteins and allow identification of this reduction product as $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{3-}$ (**3**), a synthetic analogue of the reduced protein group **1**. Inasmuch as **2** lacks any features which would tend to localize the electron added upon reduction, it is concluded that class II mixed-valence behavior is an intrinsic property of any $[Fe_2S_2(SR)_4]^{3-}$ species and probably of any species containing the planar bridged $[2Fe\text{–}2S]^{1+}$ core unit. Thus the localized electronic configuration of all Fd_{red} proteins thus far examined, which has been detected by one or more spectroscopic techniques capable of sensing lifetimes in the domain of relatively fast electron-transfer processes, is not necessarily a consequence of protein structure. The analogue **3** has as yet been obtained only in solution. The identity of the other reaction product(s) has not been ascertained but appears to be a species containing high-spin $Fe^{III}S_4$ sites.

Four types of iron–sulfur prosthetic groups, containing one to four Fe atoms, have been established in proteins. Among these the tetrahedral 1-Fe group $[Fe(S\text{–}Cys)_4]$ present in conventional rubredoxins (Rd) is structurally[2] and electronically[3] the simplest, and the 3-Fe group, having a cyclic [3Fe–3S] core of as yet incompletely defined properties, is the newest to be discovered.[4,5] The remaining two types, $[Fe_4S_4(S\text{–}Cys)_4]$[6] and $[Fe_2S_2(S\text{–}Cys)_4]$

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