of benzene. CO_2 (42 mL, 1.70 mmol) was introduced at ambient temperature through the serum-stoppered three-way stopcock with a hypodermic syringe, and the resulting benzene solution was stirred for 3 h at ambient temperature. MeI (0.11 mL, 1.70 mmol) was added, and the reaction mixture was stirred overnight at room temperature. GLPC analysis of the reaction mixture on 20% Silicone DC 550 on a Celite 545 column with tetralin as an internal standard indicated the formation of $(n\text{-Bu})_2NCO_2Me$ in a yield of 76%, which was identified by the agreement of its IR spectra and retention time of GLPC with those of the authentic sample.

Thermal Decomposition of Copper(I) *N*,*N*-Di-*n*-butylamide (3e). A solution of 5 mL of tetralin containing **3e** (0.407 g, 2.12 mmol) was gradually heated to about 110 °C where a black precipitate began to deposit. After being heated at 110 °C for 1 h, the reaction mixture was analyzed by GLPC on 20% Silicone DC 550 on a Celite 545 column with ethylbenzene as an internal standard. Di-*n*-butylamine and *N*-*n*-butylidene-*n*-butylamine were produced in 30% and 20% yields, respectively, which were identified by the agreement of their IR spectrum and retention times of GLPC with those of authentic samples.

Registry No. **1**, 75732-01-3; **3a**, 77590-45-5; **3b**, 77590-46-6; **3c**, 77590-47-7; **3d**, 71426-07-8; **3e**, 77590-48-8; **3f**, 73680-02-1; **3g**, 77590-49-9; **3h**, 77590-50-2; H_2NCO_2Me, 598-55-0; $n\text{-BuHNCO}_2Me$, 2594-21-0; $t\text{-BuHNCO}_2Me$, 27701-01-5; Et_2NCO_2Me, 4652-44-2; $(n\text{-Bu})_2NCO_2Me$, 56475-79-7; $(CH_2)_5NCO_2Me$, 1796-27-6; $O(CH_2)_4NCO_2Me$, 6906-13-4; $C_6H_5NHCO_2Me$, 2603-10-3; CO_2, 124-38-9.

Contribution from the Departments of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and Eastern Illinois University, Charleston, Illinois 61920

Crystal Structure and Molecular Geometry of $(OC)_4WPPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2\cdot CH_3CO_2C_2H_5$. Free Radical Addition of PPh_2H to a Coordinated Phosphinoalkene

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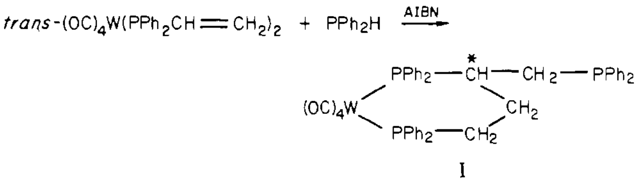
Received October 20, 1980

Base and free radical catalyzed additions of secondary phosphines to vinylphosphines are convenient syntheses for a variety of poly(tertiary phosphines).[4] The availability of starting materials limits the variety of products, however, with most containing phosphorus atoms connected by $(CH_2)_n$ units. Some variation in the backbone substituency can be introduced by carrying out addition reactions on coordinated phosphinoalkenes[5] or phosphinoalkynes.[6] The recently reported reaction of *trans*-$(OC)_4W(PPh_2CH{=}CH_2)_2$ with PPh_2H is such an example[5] (eq 1). This reaction generates a tris(tertiary



I

phosphine) (I) which is capable of forming five- or six-membered chelating rings and which contains a chiral carbon center in the backbone. Wilkinson-type catalytic systems incorporating chiral bidentate phosphines are very useful for asymmetric synthesis of optically active amino acids.[7] Furthermore, rhodium complexes of tridentate phosphorus ligands may serve as hydrogenation catalysts if the nonphosphorus ligand of the four-coordinate complex is reactive.[8]

Table I. Experimental Data for the X-ray Diffraction Study on Crystalline $(OC)_4WPPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2$

(A) Crystal Parameters at 24 °C[a]

cryst system: monoclinic
space group: $P2_1/c$ [C_{2h}^5, No. 14]
$a = 10.869$ (2) Å
$b = 17.030$ (3) Å
$c = 24.063$ (6) Å
$\beta = 92.80$ (2)°
$V = 4448.5$ (2) Å^3
$Z = 4$
ρ(calcd) = 1.49 g cm^{-3}
mol wt: 994.60

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\lambda = 0.710\,73$ Å)
monochromator: highly oriented graphite
reflcs measd: $\pm h,+k,+l$
2θ range: 3.0–45.0°
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 3.0°/min
scan width: [2θ(Mo Kα_1) − 0.7]°–[2θ(Mo Kα_2) + 0.7]°
std reflcs: 1,0,12; $\bar{6}11$; $\bar{2}$,10,0 (these were measured after each 97 reflcs; examination of the data indicated that no correction for decay was warranted)
reflcs collected: 6009 total, yielding 5844 symmetry-independent data
abs coeff: $\mu = 29.1$ cm^{-1}
ignorance factor: $p = 0.015$

[a] Unit-cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections of the forms {711}, {617}, {3,10,4}, {1,11,3}, {3,1,13}, and {1,4,15}.

NMR and IR spectra led to the postulation of structure I, but these data alone could not totally rule out other isomeric possibilities. A feature of the assignment that was particularly puzzling was that it required proposing phosphorus–phosphorus coupling through five bonds (3.6 Hz). Observation of long-range coupling is not uncommon when nuclear sites are separated by olefinic or aromatic groups but would not be expected through five aliphatic linkages.[9]

Experimental Section

A. Preparation of Sample. Crystals suitable for an X-ray diffraction study were obtained by a procedure similar to that previously reported[5] except for details of the final workup. During evaporation of the petroleum ether/ethyl acetate column chromatography eluting solvent, pale yellow crystals separated which were used in this study without the subsequent recrystallization from $MeOH/CH_2Cl_2$ as employed previously. Both NMR spectroscopy and elemental analysis results

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(2) On sabbatical leave from the State University of New York at Plattsburgh.
(3) Eastern Illinois University.
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0020-1669/81/1320-2730$01.25/0

Table II. Final Positional Parameters and Isotropic Thermal Parameters (in Å^2)

atom	*x*	*y*	*z*	*B*	atom	*x*	*y*	*z*	*B*
(A) $(OC)_4WPPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2$ Molecule									
W	0.23084 (3)	0.54202 (2)	0.30363 (1)		C(36)	0.2145 (7)	0.0392 (5)	0.4254 (3)	4.51 (16)
P(1)	0.05073 (16)	0.47309 (10)	0.25471 (7)		C(31′)	0.1929 (7)	0.2483 (4)	0.46121 (29)	3.58 (15)
P(2)	0.33131 (17)	0.40921 (10)	0.31567 (7)		C(32′)	0.0975 (8)	0.2996 (5)	0.4692 (3)	5.24 (19)
P(3)	0.18398 (18)	0.19228 (11)	0.39619 (8)		C(33′)	0.1046 (9)	0.3511 (6)	0.5153 (4)	6.92 (24)
C(1)	0.1461 (8)	0.5240 (4)	0.3755 (3)		C(34′)	0.2022 (10)	0.3478 (6)	0.5511 (4)	6.88 (24)
C(2)	0.3712 (7)	0.5868 (4)	0.3491 (3)		C(35′)	0.2969 (9)	0.2964 (6)	0.5458 (4)	6.60 (23)
C(3)	0.3202 (7)	0.5669 (4)	0.2340 (3)		C(36′)	0.2929 (7)	0.2462 (5)	0.4993 (3)	4.81 (18)
C(4)	0.1581 (7)	0.6481 (4)	0.2963 (3)		H(12)	−0.0591	0.6007	0.3136	6.0
O(1)	0.0989 (7)	0.5169 (4)	0.41626 (26)		H(13)	−0.2565	0.6599	0.3118	6.0
O(2)	0.4515 (5)	0.6124 (3)	0.37642 (25)		H(14)	−0.4145	0.6095	0.2553	6.0
O(3)	0.3721 (5)	0.5852 (4)	0.19541 (23)		H(15)	−0.3836	0.5016	0.2016	6.0
O(4)	0.1220 (5)	0.7115 (3)	0.29251 (28)		H(16)	−0.1875	0.4443	0.1983	6.0
C(5)	0.0180 (6)	0.3767 (4)	0.28616 (29)		H(12′)	0.0199	0.3355	0.1793	6.0
C(6)	0.1223 (6)	0.3173 (4)	0.29173 (28)		H(13′)	0.0639	0.3144	0.0847	6.0
C(7)	0.2247 (6)	0.3309 (4)	0.33743 (28)		H(14′)	0.1241	0.4188	0.0321	6.0
C(8)	0.2857 (6)	0.2532 (4)	0.35440 (27)		H(15′)	0.1447	0.5424	0.0680	6.0
C(11)	−0.1038 (6)	0.5186 (4)	0.25535 (27)	3.09 (14)	H(16′)	0.1052	0.5650	0.1625	6.0
C(12)	−0.1240 (7)	0.5810 (5)	0.2896 (3)	4.20 (16)	H(22)	0.5901	0.4444	0.3199	6.0
C(13)	−0.2423 (7)	0.6157 (5)	0.2890 (3)	5.00 (18)	H(23)	0.7421	0.4651	0.3908	6.0
C(14)	−0.3354 (8)	0.5858 (5)	0.2558 (3)	5.11 (18)	H(24)	0.6989	0.4454	0.4819	6.0
C(15)	−0.3167 (7)	0.5229 (5)	0.2237 (2)	4.91 (18)	H(25)	0.5027	0.4068	0.5055	6.0
C(16)	−0.2003 (7)	0.4880 (5)	0.2219 (3)	4.30 (16)	H(26)	0.3481	0.3874	0.4354	6.0
C(11′)	0.0639 (6)	0.4518 (4)	0.18038 (26)	3.33 (13)	H(22′)	0.3050	0.4216	0.1974	6.0
C(12′)	0.0475 (7)	0.3777 (5)	0.1574 (3)	4.91 (18)	H(23′)	0.3915	0.3623	0.1212	6.0
C(13′)	0.0721 (8)	0.3653 (6)	0.1008 (4)	6.13 (21)	H(24′)	0.5469	0.2712	0.1354	6.0
C(14′)	0.1076 (9)	0.4273 (6)	0.0700 (4)	6.51 (23)	H(25′)	0.6208	0.2396	0.2244	6.0
C(15′)	0.1205 (8)	0.5004 (6)	0.0909 (4)	6.01 (21)	H(26′)	0.5285	0.2931	0.3018	6.0
C(16′)	0.0975 (7)	0.5137 (4)	0.1473 (3)	4.16 (16)	H(32)	0.4491	0.1475	0.4020	6.0
C(21)	0.4541 (6)	0.4128 (4)	0.37085 (27)	3.08 (13)	H(33)	0.5572	0.0301	0.4217	6.0
C(22)	0.5716 (7)	0.4366 (4)	0.3577 (3)	4.15 (16)	H(34)	0.4444	−0.0799	0.4474	6.0
C(23)	0.6620 (7)	0.4488 (5)	0.3999 (3)	5.25 (18)	H(35)	0.2353	−0.0766	0.4471	6.0
C(24)	0.6363 (8)	0.4375 (5)	0.4535 (4)	5.60 (20)	H(36)	0.1272	0.0403	0.4259	6.0
C(25)	0.5201 (8)	0.4145 (5)	0.4676 (3)	5.26 (19)	H(32′)	0.0276	0.3005	0.4438	6.0
C(26)	0.4285 (7)	0.4026 (4)	0.42592 (30)	3.93 (15)	H(33′)	0.0403	0.3876	0.5208	6.0
C(21′)	0.4065 (6)	0.3642 (4)	0.25722 (27)	3.11 (13)	H(34′)	0.2058	0.3830	0.5817	6.0
C(22′)	0.3683 (6)	0.3836 (4)	0.20347 (29)	3.71 (15)	H(35′)	0.3638	0.2945	0.5727	6.0
C(23′)	0.4201 (7)	0.3489 (5)	0.1580 (3)	4.75 (17)	H(36′)	0.3588	0.2107	0.4939	6.0
C(24′)	0.5118 (8)	0.2954 (5)	0.1665 (4)	5.37 (19)	H(5)	−0.0089	0.3864	0.3224	6.0
C(25′)	0.5546 (8)	0.2757 (5)	0.2193 (4)	5.34 (19)	H(5′)	−0.0468	0.3532	0.2640	6.0
C(26′)	0.5013 (7)	0.3084 (4)	0.26530 (30)	4.23 (16)	H(6)	0.1605	0.3158	0.2571	6.0
C(31)	0.2787 (6)	0.1061 (4)	0.41204 (28)	3.44 (14)	H(6′)	0.0863	0.2676	0.2987	6.0
C(32)	0.4045 (8)	0.1017 (5)	0.4112 (3)	5.16 (18)	H(7)	0.1909	0.3502	0.3704	6.0
C(33)	0.4701 (8)	0.0323 (6)	0.4233 (4)	5.99 (20)	H(8)	0.3596	0.2637	0.3758	6.0
C(34)	0.4025 (8)	−0.0326 (6)	0.4377 (4)	5.94 (20)	H(8′)	0.3043	0.2250	0.3217	6.0
C(35)	0.2794 (8)	−0.0306 (6)	0.4381 (4)	6.08 (21)					
(B) Ethyl Acetate Molecule of Solvation									
EC(1)	0.7766 (11)	0.2657 (7)	0.5592 (6)		H(EC12)	0.7289	0.3055	0.5754	6.0
EC(2)	0.7163 (11)	0.2411 (6)	0.5063 (6)		H(EC13)	0.7836	0.2219	0.5836	6.0
EC(3)	0.7119 (11)	0.2285 (6)	0.4062 (5)		H(EC31)	0.6379	0.2579	0.4015	6.0
EC(4)	0.7953 (10)	0.2478 (7)	0.3622 (5)		H(EC32)	0.6931	0.1740	0.4054	6.0
EO(1)	0.6140 (9)	0.2161 (5)	0.5061 (4)		H(EC41)	0.7568	0.2353	0.3270	6.0
EO(2)	0.7770 (7)	0.2491 (4)	0.4591 (4)		H(EC42)	0.8691	0.2183	0.3675	6.0
H(EC11)	0.8563	0.2855	0.5528	6.0	H(EC43)	0.8140	0.3022	0.3636	6.0

indicated unambiguously that the molecule of ethyl acetate of solvation present in the crystallographic sample is lost on recrystallization. The solvent-free form of this compound, however, proved unsatisfactory for single-crystal analysis due to size, crystal habit, and weak diffraction properties.

B. Collection and Processing of X-ray Diffraction Data. An irregular parallelepiped of approximate dimensions 0.13 × 0.24 × 0.26 mm was cemented on a glass fiber fixed in an aluminum pin and mounted in a eucentric goniometer. Preliminary precession and cone-axis photographs indicated that the crystal was of satisfactory quality and possessed C_{2h} ($2/m$) Laue symmetry. Crystal alignment, determination of orientation matrix and unit-cell dimensions, and data collection were carried out as described previously.[10] Table I presents the details of this analysis. The centrosymmetric monoclinic space group $P2_1/c$ was uniquely indicated by the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$.

All crystallographic computations were performed with use of the Syntex XTL system, including the XTL interactive crystallographic program package[11] as modified by our research group at the State University of New York at Buffalo. Data were corrected for absorption by an empirical method based on a series of Ψ scans.[12] The reflections used to obtain the normalized absorption curves, their 2θ values, and their min:max intensity ratios were as follows: [4,1,15], 30.6°, 1.14:1; [3,1,13], 25.5°, 1.15:1; [319], 19.6°, 1.14:1; [218], 16.0°, 1.13:1.

Redundant and equivalent data were averaged ($R(I)$ = 1.80%) and were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

C. Solution and Refinement of the Structure. The analytical form[13] of the scattering factors for neutral tungsten, phosphorus, oxygen,

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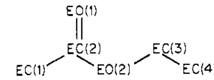
Table III. Anisotropic Thermal Parameters[a] (in Å^2)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			(A) $(OC)_4WPPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2$ Molecule			
W	2.789 (13)	2.104 (12)	3.081 (13)	0.154 (13)	0.037 (9)	0.023 (13)
P(1)	2.75 (8)	2.88 (9)	3.13 (8)	−0.04 (7)	0.05 (6)	0.15 (7)
P(2)	3.29 (9)	2.18 (8)	3.11 (8)	0.31 (7)	0.23 (7)	0.22 (7)
P(3)	3.89 (10)	2.83 (9)	3.81 (9)	−0.30 (8)	0.06 (8)	0.43 (7)
C(1)	5.5 (4)	3.2 (4)	4.1 (4)	0.2 (3)	0.8 (3)	0.1 (3)
C(2)	3.9 (4)	2.6 (3)	4.7 (4)	0.2 (3)	−0.3 (3)	0.3 (3)
C(3)	3.4 (4)	2.4 (3)	4.3 (4)	0.08 (26)	0.1 (3)	0.39 (28)
C(4)	4.1 (4)	2.8 (4)	4.7 (4)	0.4 (3)	0.58 (30)	0.6 (3)
O(1)	10.3 (5)	7.2 (4)	5.0 (3)	0.4 (3)	4.2 (3)	0.48 (28)
O(2)	5.8 (3)	4.07 (29)	7.0 (3)	−0.80 (26)	−2.54 (27)	−0.52 (26)
O(3)	4.64 (29)	6.7 (3)	4.66 (29)	−0.17 (26)	1.07 (24)	1.32 (26)
O(4)	5.6 (3)	3.04 (28)	10.1 (4)	1.04 (25)	1.03 (30)	1.20 (28)
C(5)	3.6 (4)	3.9 (4)	4.0 (4)	−0.5 (3)	−0.11 (28)	0.18 (30)
C(6)	3.9 (4)	2.3 (3)	3.9 (4)	−0.47 (28)	−0.47 (29)	−0.11 (27)
C(7)	3.6 (3)	1.88 (29)	3.5 (3)	−0.09 (26)	0.16 (27)	0.12 (26)
C(8)	3.6 (4)	2.5 (3)	3.5 (3)	0.11 (27)	−0.06 (27)	0.05 (26)
			(B) Ethyl Acetate Molecule			
EC(1)	7.5 (7)	9.0 (8)	11.3 (9)	−1.0 (6)	−0.2 (7)	−0.7 (7)
EC(2)	4.6 (6)	4.8 (5)	13.0 (10)	−1.0 (5)	−0.3 (7)	2.4 (6)
EC(3)	9.0 (8)	6.0 (6)	9.2 (8)	−1.5 (6)	−1.7 (6)	−1.4 (6)
EC(4)	6.9 (6)	10.3 (8)	8.3 (7)	−0.0 (6)	1.1 (5)	−2.2 (6)
EO(1)	9.5 (6)	10.0 (6)	13.7 (7)	−1.1 (5)	0.4 (5)	2.6 (5)
EO(2)	6.3 (4)	7.5 (4)	10.4 (6)	−0.5 (3)	2.1 (4)	−0.7 (4)

[a] The anisotropic thermal parameters enter the equation for F_c in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Table IV. Selected Interatomic Distances with Esd's (in Å)

(A) Distances for $(OC)_4WPPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2$			
W–P(1)	2.523 (2)	P(1)–C(11)	1.850 (7)
W–P(2)	2.522 (2)	P(1)–C(11′)	1.838 (7)
W–C(1)	2.025 (8)	P(2)–C(7)	1.859 (7)
W–C(2)	1.984 (8)	P(2)–C(21)	1.835 (7)
W–C(3)	2.024 (8)	P(2)–C(21′)	1.830 (7)
W–C(4)	1.977 (8)	P(3)–C(8)	1.850 (7)
C(1)–O(1)	1.135 (10)	P(3)–C(31)	1.822 (7)
C(2)–O(2)	1.152 (10)	P(3)–C(31′)	1.830 (7)
C(3)–O(3)	1.153 (10)	C(5)–C(6)	1.521 (10)
C(4)–O(4)	1.150 (10)	C(6)–C(7)	1.543 (10)
P(1)–C(5)	1.849 (8)	C(7)–C(8)	1.527 (8)
(B) Distances for Ethyl Acetate 			
EC(1)–EC(2)	1.463 (19)	EO(2)–EC(3)	1.467 (15)
EC(2)–EO(1)	1.190 (15)	EC(3)–EC(4)	1.465 (17)
EC(2)–EO(2)	1.349 (16)		

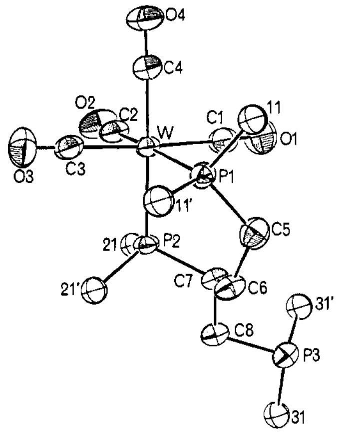


Figure 1. View of the structure of I with numbering scheme. For simplicity the phenyl groups are represented solely by the carbon atoms bonded to phosphorus. Thermal ellipsoids are drawn at the 50% level.

carbon, and hydrogen were used throughout the analysis; both real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[14] were applied to the tungsten and phosphorus atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during least-squares refinement.

Data were placed on an approximate absolute scale via a Wilson plot which also provided the overall isotropic thermal parameter B = 2.92 Å^2. The location of the tungsten atom was obtained by analysis of a three-dimensional Patterson map. Subsequent cycles of difference-Fourier syntheses and full-matrix least-squares refinement located all nonhydrogen atoms of the tungsten complex. Further refinement of these positions utilizing anisotropic thermal parameters for all atoms except for the aromatic carbon atoms led to R_F = 8.0% and R_{wF} = 8.2%. A difference-Fourier synthesis at this stage of refinement revealed the presence of a molecule of ethyl acetate for each molecule of tungsten complex. Further full-matrix least-squares refinement and the incorporation of hydrogen atoms in calculated, idealized positions (d(C–H) = 0.98 Å, B = 6.0 Å^2) led to final discrepancy indices of R_F = 4.2%, R_{wF} = 4.1%, and GOF = 1.59% for those 4804 reflections with $|F_o| > 3\sigma(|F_o|)$. The largest peaks in a final difference-Fourier synthesis were approximately 0.57 e Å^{-3} in height and were associated with the tungsten atom. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices revealed no unexpected trends.

Final positional and thermal parameters are given in Tables II and III.

Results and Discussion

Intermolecular distances and their estimated standard deviations (esd's) are shown in Table IV; interatomic angles and their esd's are given in Table V. The molecular geometry and numbering scheme are shown in Figure 1, and a stereoview is provided in Figure 2.

The original assignment of I proved to be correct. An approximate regular cis-octahedral geometry around tungsten was found. The P(1)–W–P(2) interligand angle [87.58 (6)°] deviates only slightly from 90° and the largest deviation [96.2 (2)°] was found for P(1)–W–C(3). The metal–carbon bonds trans to phosphorus are significantly shorter [1.984 (8) and 1.977 (8) Å] than those cis to phosphorus [2.025 (8) and 2.024 (8) Å], consistent with many other carbonyl complexes.[15,16]

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(14) Reference 13, pp 149–150.

Table V. Selected Interatomic Angles with Esd's (Deg)

	(A) Angles for $(OC)_4WPPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2$		
P(1)-W-P(2)	87.58 (6)	W-P(1)-C(11)	118.99 (22)
P(1)-W-C(1)	87.27 (23)	W-P(1)-C(11')	116.70 (22)
P(1)-W-C(2)	173.24 (22)	C(5)-P(1)-C(11)	100.09 (31)
P(1)-W-C(3)	95.99 (21)	C(5)-P(1)-C(11')	104.42 (32)
P(1)-W-C(4)	94.94 (22)	C(11)-P(1)-C(11')	101.90 (30)
P(2)-W-C(1)	88.78 (23)	W-P(2)-C(7)	113.76 (22)
P(2)-W-C(2)	87.97 (22)	W-P(2)-C(21)	110.34 (22)
P(2)-W-C(3)	93.45 (21)	W-P(2)-C(21')	119.68 (22)
P(2)-W-C(4)	177.47 (22)	C(7)-P(2)-C(21)	105.14 (30)
C(1)-W-C(2)	87.56 (31)	C(7)-P(2)-C(21')	103.00 (30)
C(1)-W-C(3)	176.12 (30)	C(21)-P(2)-C(21')	103.51 (31)
C(1)-W-C(4)	91.03 (31)	C(8)-P(3)-C(31)	102.61 (31)
C(2)-W-C(3)	89.35 (30)	C(8)-P(3)-C(31')	99.51 (32)
C(2)-W-C(4)	89.50 (31)	C(31)-P(3)-C(31')	103.63 (32)
C(3)-W-C(4)	86.60 (30)	P(1)-C(5)-C(6)	118.01 (50)
W-C(1)-O(1)	177.35 (70)	C(5)-C(6)-C(7)	118.03 (57)
W-C(2)-O(2)	178.69 (66)	C(6)-C(7)-C(8)	115.36 (46)
W-C(3)-O(3)	176.25 (63)	P(2)-C(7)-C(6)	110.20 (45)
W-C(4)-O(4)	176.34 (67)	P(2)-C(7)-C(8)	115.36 (46)
W-P(1)-C(5)	112.49 (23)	P(3)-C(8)-C(7)	111.58 (45)
	(B) Angles for Ethyl Acetate		
EC(1)-EC(2)-EO(1)	118.9 (12)	EO(1)-EC(2)-EO(2)	121.9 (11)
EC(1)-EC(2)-EO(2)	119.1 (11)	EO(2)-EC(3)-EC(4)	106.5 (9)

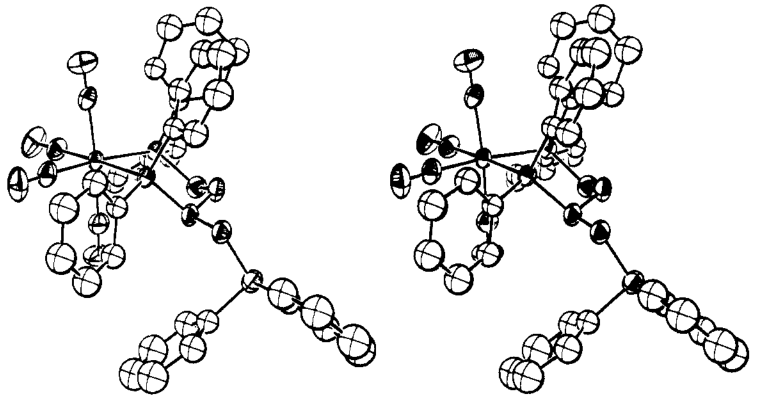

Figure 2. Stereoview of the structure of I.

The six-membered chelating ring assumes the chair arrangement with the CH_2PPh_2 substituent occupying an equatorial position which allows minimal interation with the two phenyl groups of the nearby phosphorus atom. Calculations have shown that a chair configuration is highly favored over boat and skew-boat forms in six-membered rings incorporating an octahedral system.[17] Other carbonyl complexes of group 5 ligands having six-membered rings in a chair configuration are 1,1,1,1,4,4,4,4-octacarbonyl-2,2,3,3,5,5,6,6-octamethyl-1,4-dichromia-2,3,5,6-tetraarsacyclohexane[18] and *fac*-chloro[1,3-bis(dimethylarsino)propane]tricarbonylmanganese.[19,20] The bond distances and angles within the tris(phosphine) ligand are within expected ranges.

The molecule of ethyl acetate of solvation is well removed from the tungsten complex; the closest contact is 2.64 (1) Å, between H(34) and the solvent carbonyl group oxygen atom. No significant solvent–solvent or complex–complex contacts are found.

A through-space mechanism to account for the long-range phosphorus–phosphorus coupling must be ruled out because the lone pair of P(3) cannot penetrate the four protecting groups of P(1).[21] Both the through-metal and through-ligand coupling pathways of P(3) to P(1) involve five bonds. It would not be expected that either of these pathways would produce coupling of the magnitude observed, but it is possible that small contributions from each sum to give the observed value. The ring system may impose a rigid arrangement sufficient to enhance the coupling mechanism as has been proposed for the four-bond $^{31}P-^{31}P$ coupling in $(CH_3)_2Pt[CH_3C(CH_2PPh_2)_3]$.[22] Ligands such as $PhP[CH_2CH_2CH_2P(C_6H_{11})_2]_2$ do not show phosphorus–phosphorus coupling when free or between coordinated and uncoordinated phosphorus atoms in platinum complexes in which the ligand is bidentate.[23] Similarly, unsymmetrical bis(tertiary phosphines) $RR'PCH_2CH_2CH_2PPh_2$ do not show measurable $^{31}P-^{31}P$ coupling.[24] However, the

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absence of coupling in four-bond systems cannot be used to assume it would not occur in five-bond systems.

Acknowledgment. This work was supported in part by the National Science Foundation.

Registry No. $I\cdot CH_3CO_2C_2H_5$, 77629-55-1.

Supplementary Material Available: A listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

Contribution from the Institute of General Chemistry,
Faculty of Pharmacy, University of Florence,
and the ISSECC, CNR, Florence, Italy

EPR Spectra and Zero-Field Splitting of Exchange-Coupled Copper(II)-Manganese(II) Pairs

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Received December 19, 1980

In the last few years the exchange interactions of heterodinuclear transition-metal complexes have started to be intensively investigated[1-6] and some relations between the spin Hamiltonian parameters of the individual ions and those of the pairs have been verified. In particular the **g** and **A** tensors could be satisfactorily related to those of the individual ions.[7-9] Fewer data are available for the zero-field splitting tensor, **D**, and this is unfortunate, since D is a relevant parameter in the analysis of the EPR spectra, and it yields in principle information also on the exchange and dipolar coupling.[10]

It appeared to us of interest to study some systems where the zero-field splitting tensor of both the individual ion and the pair could be measured, with the purpose to check if it is also possible to predict for **D** the values of the pair knowing those of the individual ions or vice versa.

Recently Sinn reported[11] the crystal and molecular structure and the magnetic properties of $M(prp)_2enM'(hfa)_2$ where $(prp)_2en$ is the Schiff base formed by 2-hydroxypropiophenone and ethylenediamine, hfa is hexafluoroacetylacetonate, M = Ni and Cu, and M′ = Mn, Co, Ni, and Cu. The $M(prp)_2en$ moiety is square planar, so that, when M = Ni, it is diamagnetic (Figure 1). Therefore the EPR spectra of $Ni(prp)_2enMn(hfa)_2$, Ni-Mn, should provide the spin Hamiltonian parameters of the individual manganese ion. On the other hand the exchange coupling in $Cu(prp)_2enMn(hfa)_2$, Cu-Mn, was evaluated to be $J = -26$ cm^{-1}, J being defined through the Hamiltonian $\hat{H} = J\hat{S}_1\cdot\hat{S}_2$. This means that the spins of Cu, $S_1 = {}^1/_2$, and of Mn, $S_2 = {}^5/_2$, couple to give two states, $S = 2$ and $S = 3$ separated by $\sim$78 cm^{-1}, the quintet state lying lower. The variable-temperature EPR spectra of the Cu–Mn complex therefore should allow one to determine the spin-Hamiltonian parameters of both the $S = 2$ and $S = 3$ states of the pair and compare to those of the $S = {}^5/_2$ of manganese and $S = {}^1/_2$ of copper(II).

Experimental Section

Ni-Mn and Cu-Mn were prepared as previously described.[11] Single crystals were grown by slow evaporation of dichloromethane/methanol solutions. They were found to conform to the reported crystal structures[11] and were oriented by X-ray diffraction techniques. EPR spectra at X (9 GHz) and Q band (35 GHz) were recorded with a Varian E-9 spectrometer equipped with Oxford Instruments ESR 9 and ESR 35 continuous-flow cryostats for low-temperature measurements. The single crystals were mounted on a Perspex rod and rotated by means of a goniometer. Perspex wedges were used to change the orientation of the crystal on the rod.

The calculations which yielded the spin-Hamiltonian parameters were performed with use of the matrices for $S = {}^5/_2$, $S = 2$, and $S = 3$, respectively. The transition fields were calculated by complete matrix diagonalization for varying field values to give transitions energies corresponding to $h\nu$.

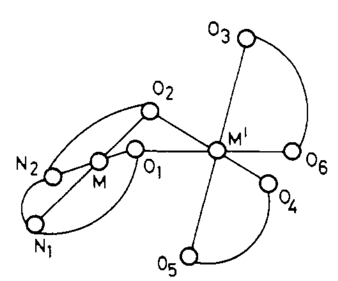

Figure 1. Sketch of the $M(prp)_2enM'(hfa)_2$ complexes.

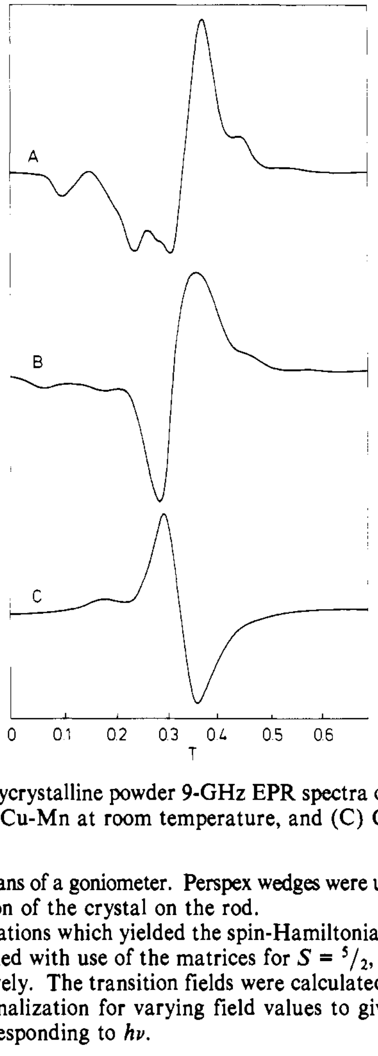

Figure 2. Polycrystalline powder 9-GHz EPR spectra of (A) Ni-Mn at 77 K, (B) Cu-Mn at room temperature, and (C) Cu-Mn at 4.2 K.

Results and Discussion

Ni-Mn. The polycrystalline powder EPR spectra (Figure 2) of Ni-Mn were recorded at both X- and Q-band frequency, in the temperature range 77–300 K. They are substantially independent of temperature and are typical[12,13] of low-sym-

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