Inorg. Chem. **1990**, *29*, 563-565 **563**

Table IV. Structural and Magnetic Data for Parallel-Planar Copper Complexes[a]

compd	$2J$, cm^{-1}	ϕ, deg	R, Å	ϕ/R, deg/Å	ref
$[Cu(Salen)]_2$ (**1**)	18	89	2.4	37.1	15
$[Cu(CH_3Sal)_2]_2$ (**2**)	8	100	2.45	40.9	16
$[Cu(8\text{-}Oquin)_2]_2$ (**3**)	−1	90.5	2.83	32.0	6
$[Cu(pyO)_2(NO_3)_2]_2$ (**4**)	10	102.9	2.44	42.2	17
$[Cu(4\text{-}CH_3pyO)_2(NO_3)_2]_2$ (**5**)	2	101.8	2.58	39.4	1e, 17b
$[Cu(piotsc)(H_2O)]_2(NO_3)_2$ (**6**)	−34	97.8	2.68	36.5	2
$(CuLZnCl_4)_2$ (**7**)	9.3	96.4	2.82	34.2	*b*

[a] Key: Salen = *N,N'*-ethylenebis(salicylaldiminate) ion; CH_3sal = *N*-methylsalicylaldiminate ion; 8-Oquin = 8-hydroxyquinolate ion; pyO = pyridine *N*-oxide; 4-CH_3pyO = 4-methylpyridine *N*-oxide; piotsc = picolinaldehyde *N*-oxide thiosemicarbazone; L = 2,2'-[1,2-ethanediylbis(nitrilomethylidyne)]bis(pyridine *N*-oxide). [b] This work.

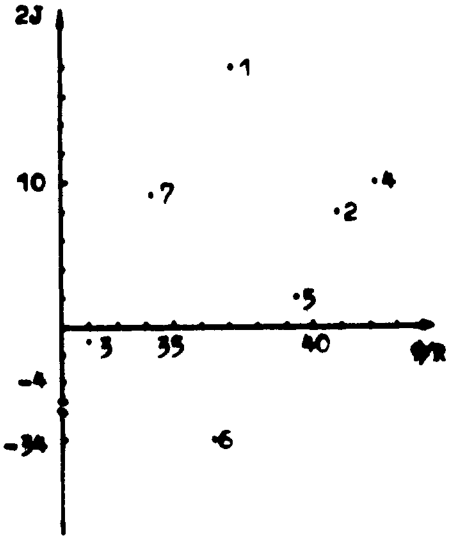

Figure 4. $2J$ and ϕ/R data for some bis(O–R) (R is aromatic ring) bridged parallel-planar copper complexes.

is the lattice-interaction parameter. This equation was used to fit the experimental data, and we found that $g = 2.09$, $J = 4.6$ cm^{-1}, and $ZJ' = -0.4$ cm^{-1}. The best fit is indicated by the solid line in Figure 3 and represents a good description of the experimental data. One may note that the g values obtained from both the best fit of the magnetic susceptibility and the EPR experiment are in good agreement with each other. The existence of weakly ferromagnetic coupling between the Cu atoms in the tetranuclear complex is also supported by the EPR spectra.

In order to understand the mechanism of exchange in the complex, we have examined the magnetic orbitals by CNDO/2 calculations. The magnetic orbital[9] obtained by calculating on a half-molecular fragment containing one Cu and one Zn and their surrounding atoms is of the form

$$\psi_A = 0.58d_{x^2-y^2}(Cu) - 0.314p_x(O(1)) + 0.505p_x(O(1')) + 0.557p_z(O(1'))$$

The other magnetic orbital, ψ_B, has the same form owing to the inversion symmetry. It is clear that there is no antiferromagnetic exchange interaction in the complex because the overlap integral between magnetic orbitals is zero.

Magnetostructural correlations for copper complexes have been studied by many researchers. It has been found that for both hydroxo-[10] and chloro-bridged[11] planar copper dimers, plotting of J versus bridging angle ϕ gives a straight line. For the parallel-planar copper complexes, it was suggested that the $2J$ be determined both by the bridging angle ϕ and by the out-of-plane bond length R.[1a-c,12] The plot of $2J$ versus ϕ/R gives a smooth curve or surface. It seems true for chloro- and bromo-bridged copper complexes.[1a-c,13] In one-atom carboxylato-bridged copper complexes, the same trend has been found.[14]

The data for some known bis(O–R) (where R is an aromatic ring) bridged parallel-planar copper complexes that have been magnetically and structurally characterized are given in Table IV. The $2J$ and ϕ/R data are shown in Figure 4. The data obviously do not lie on a smooth curve. It is clear that there is no "simple" magnetostructural correlation for such magnetically coupled copper complexes, and further studies should be needed.

Registry No. $[CuL(H_2O)](ClO_4)_2$, 121577-91-1; $(CuLZnCl_4)_2$, 124605-59-0; picolinaldehyde *N*-oxide, 7216-40-2; ethylenediamine, 107-15-3.

Supplementary Material Available: Tables SI–SIV, listing anisotropic thermal parameters, hydrogen positions and isotropic thermal parameters, bond angles and distances associated with the pyridyl ring, and experimental and calculated magnetic susceptibility data (5 pages); tables of calculated and observed structure factors (12 pages). Ordering information is given on any current masthead page.

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Reaction of $Li[(CO)_5WPPh_2]$ with $[RhCl(C_8H_{12})]_2$: Unexpected Synthesis of the Linear Trimetallic Complex $(CO)_4W(\mu\text{-}PPh_2)_2Rh(\mu\text{-}CO)_2Rh(C_8H_{12})$

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Received May 12, 1989

In pursuing our interest in the synthesis and study of the reactivity of mixed polymetallic complexes containing metals of group 6,[1,2] we have attempted the synthesis of mixed dinuclear group 6–rhodium compounds using the "bridged-assisted" synthetic pathway.[3] The literature gives examples of bimetallic complexes associating tungsten and rhodium through two diphenylphosphido groups,[4] but our aim was to have a bimetallic system bridged with only one diphenylphosphido group to minimize steric crowding around the metallic centers.

For this reason we have checked the reaction of $Li[W(CO)_5PPh_2]$ with 0.5 equiv of $[Rh(\mu\text{-}Cl)(COD)]_2$ expecting the formation of $(CO)_5W(\mu\text{-}PPh_2)Rh(COD)$. In fact the reaction is more complex than expected, and here we report the result of this study.

Results

$Li[W(CO)_5PPh_2]$ reacts with 0.5 equiv of $[Rh(\mu\text{-}Cl)(COD)]_2$ to give an orange solution. Examination of the crude product of the reaction by ^{31}P NMR spectroscopy gives evidence of the formation of two products: one singlet with satellites due to coupling with ^{183}W centered at 181 ppm corresponds to one product and a doublet of doublets with ^{183}W satellites centered at 177 ppm corresponds to the other.

These results suggest that only one of the products formed contains rhodium metal.

The two products have been separated by column chromatography. Product **1**, the minor component, is a dark red solid that corresponds to the single peak centered at 181 ppm. This information coupled with the compound's infrared spectrum (ν_{CO}(CH_2Cl_2) 2028, 1925 cm^{-1}) is consistent with the published data given for $[W(CO)_4(\mu\text{-}PPh_2)]_2$.[5]

The second product **2** is a brown solid, the analysis of which is consistent with the $WRh_2(CO)_6(PPh_2)_2(C_8H_{12})$ formulation. Its ^{31}P NMR spectrum is centered at 177 ppm and shows satellites due to coupling with the ^{183}W atom. Two coupling constants with the ^{101}Rh nucleus are observed, one with a value of 158 Hz, the other of 4.7 Hz. These data suggest that the phosphorus atoms in **2** are directly bonded to a tungsten and a rhodium atom and that they then have a long range coupling with a second atom of

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[†] Unité No. 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique.

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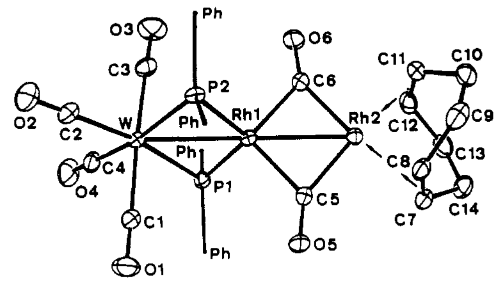

Figure 1. ORTEP plot of 2 with 30% thermal ellipsoids, showing the atom-labeling scheme. Phenyl rings have been omitted for clarity.

Table I. Selected Bond Lengths (Å) and Angles (deg) for **2** with Estimated Standard Deviations in Parentheses[a]

W-Rh(1)	2.7518 (7)	Rh(1)-C(5)	1.995 (8)
W-P(1)	2.487 (2)	Rh(1)-C(6)	1.981 (8)
W-P(2)	2.479 (2)	Rh(2)-C(5)	1.974 (8)
W-C(1)	2.034 (8)	Rh(2)-C(6)	1.973 (8)
W-C(2)	2.007 (9)	Rh(2)M(1)*	2.117 (7)
W-C(3)	2.025 (8)	Rh(2)-M(2)*	2.106 (8)
W-C(4)	1.998 (9)	Rh(2)-C(7)	2.244 (7)
Rh(1)—Rh(2)	2.6504 (8)	Rh(2)-C(8)	2.211 (8)
Rh(1)-P(1)	2.298 (2)	Rh(2)-C(11)	2.234 (8)
Rh(1)-P(2)	2.307 (2)	Rh(2)-C(12)	2.197 (8)
C(7)-C(8)	1.385 (11)	C(11)-C(12)	1.376 (12)
C(8)-C(9)	1.497 (12)	C(12)-C(13)	1.495 (12)
C(9)-C(10)	1.520 (13)	C(13)-C(14)	1.529 (12)
C(10)-C(11)	1.511 (12)	C(14)-C(7)	1.515 (11)
C(1)-O(1)	1.148 (10)	C(3)-O(3)	1.144 (11)
C(2)-O(2)	1.134 (11)	C(4)-O(4)	1.147 (11)
C(5)-O(5)	1.169 (9)	C(6)-O(6)	1.175 (10)
P(1)-W-P(2)	103.74 (7)	P(1)-Rh(1)-C(5)	105.5 (2)
P(1)-W-C(1)	88.1 (2)	P(2)-Rh(1)-C(6)	105.6 (2)
P(1)-W-C(2)	169.2 (3)	C(2)-Rh(1)C(6)	95.5 (3)
P(1)-W-C(3)	89.6 (2)	W-Rh(1)-Rh(2)	177.96 (3)
P(1)-W-C(4)	79.7 (2)	M(1)*-Rh(2)-M(2)*	85.7 (3)
P(2)-W-C(1)	94.4 (2)	M(1)*-Rh(2)-C(5)	89.9 (3)
P(2)-W-C(2)	87.0 (3)	M(1)*-Rh(2)C(6)	167.8 (3)
P(2)-W-C(3)	84.9 (2)	M(2)*-Rh(2)-C(5)	170.1 (3)
P(2)-W-C(4)	172.0 (2)	M(2)*-Rh(2)-C(6)	89.5 (3)
C(1)-W-C(2)	89.3 (3)	C(5)-Rh(2)-C(6)	96.5 (3)
C(1)-W-C(3)	177.4 (3)	C(5)-Rh(2)-C(7)	89.3 (3)
C(1)-W-C(4)	92.9 (3)	C(5)-Rh(2)-C(8)	90.5 (3)
C(2)-W-C(3)	93.2 (3)	C(5)-Rh(2)-C(11)	169.0 (3)
C(2)-W-C(4)	90.0 (4)	C(5)-Rh(2)—C(12)	153.0 (3)
C(3)-W-C(4)	87.9 (3)	C(6)-Rh(2)-C(7)	170.5 (3)
W-C(1)-O(1)	176.8 (7)	C(6)-Rh(2)-C(8)	150.5 (3)
W-C(2)-O(2)	179.0 (8)	C(6)-Rh(2)-C(11)	88.2 (3)
W-C(3)-O(3)	178.4 (8)	C(6)-Rh(2)-C(12)	90.9 (3)
W-C(4)-O(4)	177.8 (7)	C(7)-Rh(2)-C(12)	80.7 (3)
Rh(1)-C(5)-O(5)	130.4 (6)	C(8)-Rh(2)-C(11)	80.7 (3)
Rh(2)-C(5)-O(5)	145.8 (6)	Rh(1)-C(6)-O(6)	130.4 (7)
Rh(1)-C(5)-Rh(2)	83.8 (3)	Rh(2)-C(6)-O(6)	145.4 (7)
C(14)-C(7)-C(8)	124.7 (7)	Rh(1)-C(6)-Rh(2)	84.2 (3)
C(7)-C(8)-C(9)	125.3 (8)	C(10)-C(11)-C(12)	124.0 (7)
C(8)-C(9)-C(10)	115.2 (7)	C(11)-C(12)-C(13)	125.0 (8)
C(9)-C(10)-C(11)	112.8 (7)	C(12)-C(13)-C(14)	114.3 (7)
P(1)-Rh(1)-P(2)	116.06 (7)	C(13)-C(14)-C(7)	114.6 (7)

[a] M(1)* and M(2)* are respectively the midpoints of the C(7)-C(8) and C(11)-C(12) bonds.

rhodium. The proton NMR spectrum of **2** confirms the presence of four phenyl groups and one cyclooctadiene molecule, and evidence for the presence of bridging carbonyl groups is given by infrared spectroscopy. The precise nature of **2** has been determined by an X-ray crystallography structure determination. An ORTEP view of **2** is shown in Figure 1, while bond lengths and bond angles of interest can be found in Table I. The molecule consists of a trimetallic WRh_2 chain, the W-Rh(1) bond being bridged by two diphenylphosphido ligands and the Rh(1)-Rh(2) bond by two carbonyl groups.

Table II. Crystallographic Data

chem formula: $C_{38}H_{32}O_6P_2Rh_2W$	fw 1036.3
a = 10.685 (1) Å	space group: $P2_1/n$ (No. 14)
b = 18.873 (3) Å	λ = 0.71073 Å
c = 18.232 (2) Å	ρ_{calcd} = 1.873 g cm^{-3}
β = 91.74 (1)°	μ = 41.9 cm^{-1}
V = 3674.9 Å^3	transm coeff = 0.79-1.00
Z = 4	$R(F_o)$ = 0.031
T = 20 °C	R_w = 0.036

Contrary to the case for the $[(CO)_4W(\mu\text{-}PPh_2)Rh(\mu\text{-}CO)]_2$ (**3**) complex,[4] the W-Rh-Rh chain is linear and the $(Rh(\mu\text{-}CO))_2$ unit is planar. The angle between Rh(1), Rh(2), C(5), C(6) and W, Rh(1), P(1), P(2) planes is 98°.

The W-Rh(1) distance is slightly shorter than that in **3** but lies within accepted distance for a W-Rh single bond.[4,6,7] The Rh(1)-Rh(2) distance is also normal for a Rh-Rh single bond and compares well to the values found in **3**[4] or $[Rh(PPh_3)_2(\mu\text{-}CO)]_2$.[8]

The geometry around tungsten, without consideration of the W-Rh bond, is nearly octahedral, and the P(1)-W-P(2) angle is slightly more opened than in **3**.

The cyclooctadiene has normal structural parameters for this ligand,[9] and the centers of the double bonds are in the same plane as the $[Rh(\mu\text{-}CO)]_2$ core.

To summarize, the reaction of $Li[W(CO)_5(PPh_2)]$ with 0.5 equiv of $[RhCl(COD)_2]$ is a complex reaction that leads to the unexpected formation of the trimetallic $(CO)_4W(\mu\text{-}PPh_2)_2Rh(\mu\text{-}CO)_2Rh(COD)$ (**2**). The mechanism of this reaction is quite obscure as it implies a complete redistribution of ligands, $W(CO)_6$ and $[W(CO)_4(\mu\text{-}PPh_2)]_2$ complexes being identified as by products. Nevertheless, the yield of **2** (52% on the basis of rhodium) is surprisingly good.

We have checked the reactivity of **2** toward hydrogen and carbon monoxide, but these reactions lead to decomposition with metal deposition and only $W(CO)_6$ and $[(CO)_4W(\mu\text{-}PPh_2)]_2$ have been detected in solution.

Experimental Section

All manipulations were carried out under an inert atmosphere by use of standard Schlenk techniques. Infrared spectra were recorded in CH_2Cl_2 solutions on a Perkin-Elmer 225 instrument. ^1H and ^{31}P NMR spectra were recorded on a Bruker AC200 spectrometer.

Preparation of $(CO)_4W(\mu\text{-}PPh_2)_2Rh(\mu\text{-}CO)_2Rh(COD)$ (2). To 0.83 g of $W(CO)_5(PPh_2H)$[10] (1.62 mmol) dissolved in 10 mL of THF was added 1.2 mL of BuLi 1.48 M in hexane (10% excess) at 0 °C. To this solution 0.4 g of $[Rh(\mu\text{-}Cl)(COD)]_2$ (0.81 mmol) was added, and the solution was stirred for 15 min at 0 °C and then 15 min at room temperature.

Evaporation of the brown solution and chromatography of the residue on a silica column with a 80/20 hexane/dichloromethane mixture gave successively $W(CO)_6$, $[W(CO)_4(\mu\text{-}PPh_2)]_2$ (**1**) in trace amounts, and **2**. **2** was recrystallized in a CH_2Cl_2/MeOH mixture at -20 °C, and 0.44 g (52% yield on the basis of rhodium) of brown crystals was isolated.

Anal. Calcd for $C_{38}H_{32}O_6P_2Rh_2W$: C, 44.02; H, 3.09; P, 5.98; Rh, 19.88; W, 17.76. Found: C, 44.17; H, 3.27; P, 5.47; Rh, 18.6; W, 15.4. IR (ν_{CO}; CH_2Cl_2 solution): 2048 s, 1957 sh, 1945 s, 1825 w, 1795 m cm^{-1}. ^1H NMR ($CDCl_3$ solution): 7.32 m (C_6H_5), 5.17 m (4 H), 2.51

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Table III. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	*x*/*a*	*y*/*b*	*z*/*c*
W	0.28322 (3)	0.56915 (2)	0.25327 (2)
Rh(1)	0.41513 (6)	0.67772 (3)	0.19097 (3)
Rh(2)	0.54838 (6)	0.77899 (3)	0.12970 (3)
P(1)	0.2000 (2)	0.6768 (1)	0.1900 (1)
P(2)	0.5134 (2)	0.5811 (1)	0.2447 (1)
C(1)	0.2614 (8)	0.5165 (4)	0.1564 (4)
O(1)	0.2433 (6)	0.4866 (3)	0.1023 (3)
C(2)	0.3164 (9)	0.4764 (5)	0.3040 (5)
O(2)	0.3335 (8)	0.4241 (4)	0.3333 (4)
C(3)	0.3059 (8)	0.6257 (5)	0.3471 (4)
O(3)	0.3184 (7)	0.6591 (4)	0.3992 (4)
C(4)	0.1017 (8)	0.5610 (4)	0.2753 (4)
O(4)	−0.0019 (6)	0.5579 (4)	0.2897 (4)
C(5)	0.4607 (8)	0.6958 (4)	0.0873 (4)
O(5)	0.4366 (6)	0.6638 (3)	0.0338 (3)
C(6)	0.5026 (8)	0.7619 (4)	0.2322 (4)
O(6)	0.5100 (6)	0.7832 (4)	0.2928 (3)
C(7)	0.5878 (8)	0.8164 (4)	0.0159 (4)
C(8)	0.6864 (7)	0.7750 (5)	0.0419 (4)
C(9)	0.8075 (8)	0.8025 (5)	0.0741 (5)
C(10)	0.7958 (8)	0.8660 (5)	0.1248 (5)
C(11)	0.6809 (8)	0.8626 (4)	0.1710 (4)
C(12)	0.5678 (8)	0.8930 (4)	0.1513 (5)
C(13)	0.5415 (8)	0.9330 (5)	0.0817 (5)
C(14)	0.5889 (9)	0.8966 (4)	0.0129 (5)
C(15)	0.1060 (5)	0.6681 (3)	0.1050 (3)
C(16)	0.0149 (5)	0.6158 (3)	0.0950 (3)
C(17)	−0.0534 (5)	0.6114 (3)	0.0287 (3)
C(18)	−0.0305 (5)	0.6594 (3)	−0.0276 (3)
C(19)	0.0607 (5)	0.7117 (3)	−0.0175 (3)
C(20)	0.1290 (5)	0.7160 (3)	0.0488 (3)
C(21)	0.1153 (4)	0.7385 (3)	0.2471 (3)
C(22)	0.1825 (4)	0.7809 (3)	0.2971 (3)
C(23)	0.1191 (4)	0.8245 (3)	0.3453 (3)
C(24)	−0.0115 (4)	0.8258 (3)	0.3435 (3)
C(25)	−0.0787 (4)	0.7835 (3)	0.2935 (3)
C(26)	−0.0153 (4)	0.7398 (3)	0.2453 (3)
C(27)	0.6115 (4)	0.5279 (3)	0.1855 (2)
C(28)	0.7235 (4)	0.4967 (3)	0.2099 (2)
C(29)	0.7962 (4)	0.4591 (3)	0.1610 (2)
C(30)	0.7569 (4)	0.4527 (3)	0.0876 (2)
C(31)	0.6448 (4)	0.4839 (3)	0.0632 (2)
C(32)	0.5721 (4)	0.5215 (3)	0.1122 (2)
C(33)	0.6081 (5)	0.5923 (3)	0.3296 (3)
C(34)	0.5760 (5)	0.5574 (3)	0.3938 (3)
C(35)	0.6443 (5)	0.5698 (3)	0.4590 (3)
C(36)	0.7447 (5)	0.6170 (3)	0.4599 (3)
C(37)	0.7768 (5)	0.6519 (3)	0.3958 (3)
C(38)	0.7085 (5)	0.6396 (3)	0.3306 (3)

m (8 H) ppm. ^{31}P NMR (CDCl$_3$ solution): 177 dd ppm (J_1 = 158 Hz; J_2 4.7 Hz J_{PW} 167.3 Hz).

X-ray Structure Analysis. The experimental parameters are listed in Table II. The crystal was sealed on a glass fiber and transferred to a CAD4 Enraf-Nonius diffractometer automated with a Microvax 2000 computer.

The unit cell was refined by using 25 reflections in the 2θ range of 22–26°. A total of 6822 intensity data, up to 2θ = 50°, were collected in the $\theta/2\theta$ scan mode (scan width 0.80° + 0.35° tan θ, scan speed 1.1–8.4° min^{-1}). A set of three standard reflections was measured every 2 h of exposure time, with no noticeable change in intensity observed during the collection. Lorentz–polarization and empirical absorption[12] corrections were made with SDP.[13]

The structure was solved by a Patterson map calculation, and the refinement and difference-Fourier processes were completed with SHELX 76[14] using 4279 reflections having $I > 3\sigma(I)$ out of the 6462 independent ones. The atomic scattering factors are those of ref 15 for heavy atoms and those of ref 16 for hydrogens. Full-matrix least-squares techniques were used with phenyl rings refined as isotropic rigid groups (C–C = 1.395 Å). All H atoms were observed but introduced in calculations in constrained geometry (C–H = 0.97 Å) with a temperature factor U = 0.07 Å^2, kept fixed. All other atoms were refined anisotropically. The refinement converged with a maximum shift/esd of 0.006 on the final cycle with 274 variable parameters. A good fit of S = 1.35 for the data using the weighting scheme $w = [\sigma^2(F_o) + 0.0002F_o^2]^{-1}$ was obtained. The maximum residual peak was near the W atom at 0.82 e Å^{-3}. Fractional atomic coordinates are given in Table III.

Supplementary Material Available: For **2**, tables of hydrogen atom coordinates, anisotropic thermal parameters, all bond distances and bond angles, and least-squares plane equations (5 pages); a table of calculated and observed structure factors (6 pages). Ordering information is given on any current masthead page.

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Photochemical Reactions of the Binuclear Platinum(II) Diphosphite Complex $Pt_2(P_2O_5H_2)_4^{4-}$ with Disubstituted Silanes

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The photochemical properties of the intensity luminescent, binuclear platinum(II) diphosphite complex $Pt_2(P_2O_5H_2)_4^{4-}$ (Pt$_2$) have attracted much interest in recent years.[1-10] The long microsecond lifetime (τ = 9.8 μs) of ^{3}Pt$_2$* makes it feasible to carry out chemical reactions with this triplet excited state.[3-9] It was reported that the triplet excited state ^{3}Pt$_2$* has a unique reactivity to transfer hydrogen atoms from several organic substrates with relatively weak C–H bonds.[8-10] Hydrogen atom transfer, RH + ^{3}Pt$_2$* → R$^\bullet$ + Pt$_2$H was proposed by Roundhill to be the primary photoprocess in the photoinduced reactions of ^{3}Pt$_2$* with RH. Gray et al.[11-13] recently reported the results of hydrogen atom transfer from triaryl- or trialkyl-substituted organometallic hydrides of Sn, Ge, and Si by ^{3}Pt$_2$* and thereby provided support for Roundhill's proposal.

In order to explore the reactions of ^{3}Pt$_2$* with bonds other than C–H for their potential applications, the photochemical reactions of Pt$_2$ with disubstituted silanes R^{1}R^{2}SiH$_2$ have been preliminarily examined. This work provides further support for the hydrogen

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