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HAL Id: hal-03545054

<https://hal.science/hal-03545054>

Submitted on 27 Jan 2022

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REACTIONS BETWEEN $W_2I_4(CO)_8$ AND PHOSPHINES UNDER FORCING CONDITIONS: ATTEMPTED DECARBONYLATION TO TUNGSTEN(II) DIMERS WITH QUADRUPLE METAL–METAL BOND—X-RAY MOLECULAR STRUCTURE OF $WI_2(CO)(dppm)_2$

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(Received 18 July 1986; accepted 24 October 1986)

Abstract—The reactions of $W_2I_4(CO)_8$ with bis(diphenylphosphino)methane (dppm) and PMe_3 have been studied under forcing conditions. From the dppm reaction a monocarbonyl compound has been isolated, which crystallizes as $3WI_2(CO)(dppm)_2 \times 2$ toluene. Crystal data: space group $C2/c$, $a = 31.141(8)$, $b = 25.447(7)$, $c = 20.135(6)$ Å, $\beta = 104.89(4)^\circ$, $V = 15420(20)$ Å³, $Z = 4$, $R = 0.0538$ for 4367 data with $F_o^2 > 3\sigma(F_o^2)$. The PMe_3 reaction afforded $WI_2(CO)_2(PMe_3)_3$ as the major product. No derivatives containing a metal–metal quadruple bond were detected in solution.

Recent investigations carried out in this Laboratory^{1–4} led to the discovery of a new reaction, namely thermal decarbonylation of $Mo_2I_4(CO)_8$ in the presence of phosphines, which is at the same time a new reactivity path for compounds of the $Mo_2X_4(CO)_8$ type and a new synthetic method for $Mo_2X_4L_4$ or $Mo_2X_4(L-L)_2$ compounds with a metal–metal bond.

In an attempt to extend this method to the analogous tungsten complexes, the thermal reaction of $W_2I_4(CO)_8$ ⁵ with selected phosphines was carried out. PMe_3 and bis(diphenylphosphino)methane (dppm), i.e. the phosphines which gave the best results with the molybdenum system,^{1,2} were chosen. Quadruply bonded tungsten dimers could not be obtained and the isolated products were carbonyl complexes related to intermediates of the molybdenum reactions. These products and the mechanism of their formation are discussed here.

EXPERIMENTAL

All operations were carried out by standard Schlenk tube techniques under an atmosphere of

purified argon. Solvents were dehydrated by conventional methods and distilled under dinitrogen. Instruments used were: IR, Perkin–Elmer mod 783; UV–visible, Cary 17. Solution IR spectra were recorded on expanded abscissa and calibrated with both $CO_{(g)}$ and $H_2O_{(g)}$. Elemental analyses were by Galbraith Laboratories Inc., Knoxville, Tennessee. $W_2I_4(CO)_8$ ⁵ and PMe_3 ⁶ were prepared by known procedures. Dppm was purchased from Strem Chemicals and used without further purification.

Reaction of $W_2I_4(CO)_8$ with dppm

$W_2I_4(CO)_8$ (0.52 g, 0.47 mmol) and dppm (0.40 g, 1.04 mmol) were dissolved in 50 cm³ of toluene to produce, after gas evolution, an orange solution with IR bands at 2035m, 1962s, 1938m, 1908m and 1856w cm⁻¹. The solution was then refluxed and the reaction monitored by IR in the carbonyl stretching region. After ca 24 h all of the bands had practically disappeared and a new, weak band at ca 1775 cm⁻¹ had grown. The mixture was filtered while hot and slowly cooled to room temperature. The red crystals that formed (compound 1, ca 72 mg) were decanted, washed with *n*-hexane and dried *in vacuo*. Found: C, 50.4; H, 3.8. Calc. for $C_{167}H_{148}I_6O_3P_{12}W_3$: C, 51.6; H, 3.8%. IR (Nujol mull) (cm⁻¹): 1765s,

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1590w, 1575w, 1435m, 1355w, 1315w, 1160w, 1085m, 1030w, 1005w, 975w, 845w, 790m, 745s, 735s, 720m, 690s, 615w, 595w, 520m, 505m, 480m, 450w, 420m; (CH₂Cl₂ solution) (cm⁻¹): 1778. Subsequent work-up of the mother solution did not lead to the isolation of any pure crystalline material. UV-visible spectroscopy on this solution did not show any band in the 600–900-nm region.

Reaction of W₂I₄(CO)₈ with PMe₃

W₂I₄(CO)₈ (0.75 g, 0.69 mmol) was treated in 20 cm³ of toluene with 0.30 cm³ of PMe₃ (3.0 mmol). A yellow solution and a flocculent yellow precipitate were obtained after gas evolution. The solution had IR bands at 2071w, 2046w, 2014s, 1936s, 1907s and 1888vs cm⁻¹. The mixture was then warmed to reflux and at the same time irradiated with a UV-mercury lamp. The solid gradually dissolved and the color changed to red within 12 h. This solution had IR bands at 2017w, 1926vs, ca 1900w (sh), 1827vs and 1731m cm⁻¹. Color and IR spectrum did not change upon further treatment for an additional 24 h. UV-visible spectroscopy did not show any band in the 600–900-nm region. After evaporation to dryness, the residue was washed several times with hot *n*-hexane to give red solutions whose prominent IR band was at 1730 cm⁻¹, and to leave a yellow microcrystalline material. This was recrystallized by dissolution in toluene and slow diffusion of *n*-hexane to give large orange crystals (compound **2**, yield 0.33 g). Found: C, 18.7; H, 3.8. Calc. for C₁₁H₂₇I₂O₂P₃W: C, 18.3; H, 3.8%. IR (Nujol mull) (cm⁻¹): 1915s, 1820vs, 1430m, 1425m, 1415w, 1305m, 1300w, 1285m, 1275ms, 950s, 870w, 860w, 730m, 670w, 585w, 570w, 515w, 490w, 445w; (toluene solution) (cm⁻¹): 1925s, 1830s (asymmetric).

X-ray crystallography for compound **1**

Data collection and reduction were carried out by routine procedures. A semi-empirical absorption correction was applied according to the method described by North *et al.*⁷ The structure solution and the early stages of refinement were performed with the Enraf-Nonius SDP software. On the basis of systematic absences, the space group could be either *Cc* or *C2/c*. Direct methods on the non-centrosymmetric space group showed three independent and equivalent arrangements of heavy atoms, which were initially assigned the WI₃ formulation. The positional parameters were in agreement with an extra symmetry element, this being

a C₂-axis passing through a W and an I atom of one of the three WI₃ groupings. Refinement was thus attempted in the *C2/c* space group, which led to correct development of the structure. All iodine atoms which were not in a special position were first refined at full occupancy but I(2), I(3) and I(4) refined with unusually high thermal parameters. Chemical information and elemental analyses suggested that this compound might be a di-iodide derivative of tungsten; we therefore considered the possibility of having, in each independent molecule, one iodide atom disordered over two mutually *trans* positions. Assignment of a 0.5 occupancy factor to the above mentioned iodine atoms led to correct refinement. Subsequent alternate difference Fourier maps and least-squares full-matrix refinements showed the positions of all the atoms of the dppm ligands and the carbonyl carbon atoms. The latter ones were refined at half occupancy. The *R* factor was 0.070. The carbonyl oxygen atoms were not located on the difference Fourier map. Since they were expected to be at about the same position as the iodine atoms, they were introduced in the atom list starting with the same positions as those of the iodine atoms. Subsequent refinement was performed with the SHELX-76 package of programs. The phenyl rings were constrained to be perfect hexagons (C—C = 1.395 Å) and the C—O distances were restrained to a value of 1.14(2) Å, which is the distance found for the same bond in MoI₂(CO)(dmpm)₂[dmpm = bis(dimethylphosphino)methane], having a geometry similar to that of the present compound.³ Isotropic refinement converged to *R* = 0.068. All the atoms were then allowed to behave anisotropically and refined. The carbonyl carbon and oxygen atoms did not refine well, most probably because of high correlation with the iodine atoms, and they were therefore left isotropic. At this point, the difference Fourier map showed peaks ascribable to a toluene molecule in a general position of the lattice, with the methyl groups disordered over two positions at bonding distance to two *ortho* carbons of the ring. Independent refinement of all parameters led to instability. To avoid this, the toluene ring was constrained to be a perfect hexagon (C—C = 1.395 Å), the methyl groups restrained at 1.47(10) Å from the corresponding ring atoms and with a constraint on their occupancies such that the sum of these be equal to 1. Finally the isotropic thermal parameters of all the carbon atoms of the toluene molecule were constrained to the same value, which was refined. Final refinement converged to *R* = 0.0538 (*R*_w = 0.0670). Significant crystal data are reported in Table 1, while selected bond distances and angles are reported in Table 2.

Table 1. Crystal data for $3WI_2(CO)(dppm)_2 \times 2$ toluene

Formula	$C_{167}H_{148}I_6O_3P_{12}W_3$
Formula weight	3887.7
Space group	$C2/c$
Systematic absences	$h0l: l \neq 2n; hkl: h+k \neq 2r$
a (Å)	31.141(18)
b (Å)	25.447(7)
c (Å)	20.135(6)
α (°)	90
β (°)	104.89(4)
γ (°)	90
V (Å ³)	15420(20)
Z	4
d_{calc} (g cm ⁻³)	1.675
Crystal size (mm)	0.1 × 0.2 × 0.4
μ (Mo- K_α) (cm ⁻¹)	36.437
Data collection instrument	CAD-4
Radiation (monochromated in incident beam)	Mo- K_α ($\lambda_\alpha^- = 0.71073$ Å)
Orientation reflections, number, range (2θ)	25, 18–25
Temperature (°C)	20
Scan method	ω
Data collection range [2θ (°)]	4–45
Number of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	4367
Number of parameters refined	679
Transmission factors (max, min)	99.94, 91.80
R^a	0.0538
R_w^b	0.0670
Quality-of-fit indicator ^c	1.383
Largest shift/esd, final cycle	0.255
Largest peak (e Å ⁻³)	0.764

$$^a R = \Sigma \|F_o\| - |F_c| / \Sigma |F_o|.$$

$$^b R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|).$$

$$^c \text{Quality-of-fit} = [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}.$$

RESULTS AND DISCUSSION

The reaction of $W_2I_4(CO)_8$ with phosphines and diphosphines had already been the subject of several studies.^{5,8,9} Dppm was one of the ligands employed:⁸ its reaction was shown to lead to the formation of $WI_2(CO)_3(dppm)$ and $WI_2(CO)_2(dppm)_2$ with 2 and 4 equivalents, respectively, per tungsten dimer at room temperature, and a reflux treatment of the dicarbonyl derivative in $CHCl_3$ gave rise to the formation of *trans*- and *cis*- $[WI(CO)_2(dppm)_2]I$.⁹

We used, for our reaction, a solvent (toluene) with a higher boiling point and less polarity than that used by Colton and Rix.⁹ In agreement with their findings, we obtained a mixture of WI_2

$(CO)_3(dppm)$ (bands at 2035m, 1962s and 1908m cm^{-1} ; cf. with 2030m, 1960s, 1935m and 1910m cm^{-1} in acetone⁹) and small amounts of $WI_2(CO)_2(dppm)_2$ (bands at 1938m and 1856w cm^{-1} ; cf. with 1940s and 1855s in CH_2Cl_2 or $CHCl_3$ ⁸) at room temperature; the appearance of the dicarbonyl derivative is presumably due to the small excess of the diphosphine over the 1:2 stoichiometry. When, however, the solution was refluxed, we obtained neutral compounds. $WI_2(CO)(dppm)_2$ (**1**), not previously reported, was obtained in low yields; other toluene-soluble, non-carbonyl-containing materials were also present but we were not able to isolate them in crystalline form. The lack of a visible absorption band in the 600–900-nm region, however, rules out the possibility

Table 2. Selected bond distances (Å) and angles (°), and their estimated standard deviations, for $3Wl_2(CO)(dppm)_2 \times 2$ toluene^a

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
W1	I1	2.876(2)	W2	P6	2.543(6)	P4	C70	1.86(2)
W1	I2	2.980(7)	W2	C6	1.73(6)	P4	C80	1.82(2)
W1	I3	2.984(5)	P1	C1	1.86(2)	P5	C5	1.88(2)
W1	P1	2.546(7)	P1	C10	1.81(2)	P5	C90	1.82(2)
W1	P2	2.562(6)	P1	C20	1.80(2)	P5	C100	1.78(2)
W1	P3	2.560(6)	P2	C1	1.87(2)	P6	C5	1.80(2)
W1	P4	2.552(7)	P2	C30	1.83(2)	P6	C110	1.90(3)
W1	C3	1.79(5)	P2	C40	1.829(15)	P6	C120	1.78(2)
W1	C4	1.85(5)	P3	C2	1.85(2)	O3	C3	1.08(7)
W2	I4	2.985(6)	P3	C50	1.82(2)	O4	C4	1.11(11)
W2	I5	2.876(3)	P3	C60	1.800(15)	O6	C6	1.09(9)
W2	P5	2.551(6)	P4	C2	1.86(2)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
I1	W1	I2	85.5(1)	P4	W1	C3	97(2)
I1	W1	I3	85.0(1)	P4	W1	C4	89(2)
I1	W1	P1	75.2(1)	I4	W2	I5	85.2(1)
I1	W1	P2	138.7(1)	I4	W2	P5	84.2(2)
I1	W1	P3	139.0(2)	I4	W2	P5'	93.3(2)
I1	W1	P4	75.3(1)	I4	W2	P6	87.2(2)
I1	W1	C3	91(1)	I4	W2	P6'	100.1(2)
I1	W1	C4	89(1)	I4	W2	C6'	171(2)

Atom 1	Atom 2	Atom 3	Angle
W1	P3	C2	96.0(6)
W1	P3	C50	124.1(6)
W1	P3	C60	124.3(7)
C2	P3	C50	104(1)
C2	P3	C60	104(1)
C50	P3	C60	100.8(9)
W1	P4	C2	96.0(7)
W1	P4	C70	127.3(8)

Reactions between $W_2I_4(CO)_8$ and phosphines under forcing conditions

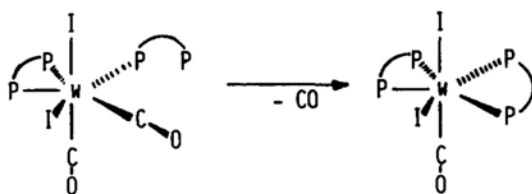
I2	W1	P1	94.1(2)	I5	W2	P5	75.2(2)	W1	P4	C80	119.4(6)
I2	W1	P2	99.9(2)	I5	W2	P6	138.8(1)	C2	P4	C70	105.(1)
I2	W1	P3	86.9(2)	I5	W2	C6	87.(2)	C2	P4	C80	103.6(9)
I2	W1	P4	84.4(2)	P5	W2	P5'	150.5(2)	C70	P4	C80	102.(1)
I2	W1	C3	176.(2)	P5	W2	P6	63.7(2)	W2	P5	C5	94.7(7)
I3	W1	P1	83.4(2)	P5	W2	P6'	145.7(2)	W2	P5	C90	118.7(6)
I3	W1	P2	87.2(2)	P5	W2	C6	88.(2)	W2	P5	C100	126.6(7)
I3	W1	P3	100.3(2)	P5	W2	C6'	90.(2)	C5	P5	C90	104.(1)
I3	W1	P4	93.4(2)	P6	W2	P6'	82.4(2)	C5	P5	C100	105.4(9)
I3	W1	C3	7.(1)	P6	W2	C6	89.(2)	C90	P5	C100	104.(1)
I3	W1	C4	173.(1)	P6	W2	C6'	96.(2)	W2	P6	C5	97.0(7)
P1	W1	P2	63.6(2)	W1	P1	C1	97.9(7)	W2	P6	C110	123.1(6)
P1	W1	P3	145.6(2)	W1	P1	C10	126.5(8)	W2	P6	C120	124.8(7)
P1	W1	P4	150.5(2)	W1	P1	C20	118.0(7)	C5	P6	C110	103.(1)
P1	W1	C3	82.(2)	C1	P1	C10	103.8(9)	C5	P6	C120	102.2(9)
P1	W1	C4	91.(2)	C1	P1	C20	102.(1)	C110	P6	C120	102.(1)
P2	W1	P3	82.3(2)	C10	P1	C20	104.6(9)	P1	C1	P2	92.3(9)
P2	W1	P4	145.8(2)	W1	P2	C1	97.1(7)	P3	C2	P4	93.8(9)
P2	W1	C3	81.(1)	W1	P2	C30	125.4(8)	W1	C3	O3	159.(5)
P2	W1	C4	95.(2)	W1	P2	C40	122.9(8)	W1	C4	O4	165.(6)
P3	W1	P4	63.9(2)	C1	P2	C30	103.3(9)	P5	C5	P6	93.7(9)
P3	W1	C3	97.(2)	C1	P2	C40	103.(1)	W2	C6	O6	162.(6)
P3	W1	C4	87.(1)	C30	P2	C40	101.(1)				

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

that the quadruply bonded dimer $W_2I_4(dppm)_2$ was present.*¹⁰

Although not certain, it would seem that, upon reflux, $WI_2(CO)_3(dppm)$ gives rise to the unidentified non-carbonyl materials, presumably containing a dppm/W ratio of 1, while $WI_2(CO)_2(dppm)_2$ produces compound **1**. A few complexes with a stoichiometry similar to that of $WI_2(CO)_2(dppm)_2$ have been structurally characterized {e.g. $MoCl_2(CO)_2(dpam)_2$,¹¹ $MoBr_2(CO)_2(dpam)_2$,¹² [dpam = bis(diphenylarsino)methane], $MoCl_2(CO)_2(dppm)_2$ ¹¹ and $MoI_2(CO)_2(dppm)_2$ ¹³} and found to be seven-coordinate with one chelating and one monodentate phosphine. By assuming that $WI_2(CO)_2(dppm)_2$ also has such a structure, the formation of **1** can easily take place by chelation of the second diphosphine *via* preliminary dissociation of a CO ligand (see Scheme 1). In the thermal treatment carried out by Colton and Rix,⁸ on the other hand, the substitution of one iodide ligand occurs, presumably because of the higher polarity of the solvent.

The crystal structure of compound **1** exhibits two independent molecules of $WI_2(CO)(dppm)_2$, one in a general position and one located on a C_2 -axis, which passes through W(2) and I(5). One molecule of toluene is also present in the asymmetric unit, so that the composition of the crystalline material is $3WI_2(CO)(dppm)_2 \times 2$ toluene. Figure 1 shows a view of the molecule which is on the general position. Both independent molecules show the same geometry around tungsten, which is fairly close to that of an ideal pentagonal bipyramid, and have identical structural parameters within the experimental error. One iodide ion and the two diphosphine ligands are in the equatorial plane, and the second iodide ion and the carbonyl ligand are in the axial positions. The symmetry imposes a 50:50 disorder of the axial iodide and carbonyl ligands in the molecule lying on the C_2 -axis. In the other molecule, although this is not required by symmetry, the same ligands were also found to be 50:50 disordered among the two axial positions. Figure 1 shows only one of the two orientations, for clarity. This result can be easily explained by considering the presence of eight bulky phenyl groups which completely surround the I-W-CO core of the molecule. The packing of the molecules



Scheme 1.

in the crystal is expected to be dominated by the van der Waals' interactions of the phenyl groups. The random disorder of the two possible orientations shows that the arrangement of the axial I-W-CO system does not appreciably influence the energy of the crystal.

The molecular structure is the same as that found³ for $MoI_2(CO)(dmpm)_2$. The "bite" angles of the diphosphines in **1** are a little smaller [63.6(2), 63.9(2) and 63.7(2)°, compared with 65.7(2) and 66.1(2)° for $MoI_2(CO)(dmpm)_2$], perhaps because of steric repulsion between the phenyl groups. The W—I distance, as expected,¹⁴ is larger for the axial bonds [2.980(7), 2.984(5) and 2.985(6) Å] than for the equatorial ones [2.876(2) and 2.876(3) Å]. The W—P bond lengths are all close to 2.55 Å, which is *ca* 0.05 Å longer than those of the corresponding Mo—dmpm complex.³

It is interesting to compare the reactivity of $W_2I_4(CO)_8$ towards dppm with that of the corresponding molybdenum system. The reaction of $Mo_2I_4(CO)_8$ with dppm (1:2 molar ratio) under forcing conditions afforded $Mo_2I_4(dppm)_2$ (Mo—Mo) in high yields.² No similar compound appears to be formed from $W_2I_4(CO)_8$. Also, $MoI_2(CO)_2(dppm)_2$ was found to decompose in refluxing toluene and no formation of $MoI_2(CO)(dppm)_2$, analogous to **1**, could be observed.^{3,13} Instead, such a decomposition reaction seemed to produce $Mo_2I_4(dppm)_2$ upon loss of diphosphine and CO. In the tungsten reaction, on the other hand, compound **1** was produced, which seemed to be rather stable in such conditions. It might be that the presumably higher energies of the W—P, W—I and W—CO bonds with respect to those of the Mo—P, Mo—I and Mo—CO bonds are capable of thermodynamically or kinetically stabilizing a highly crowded structure such as that of compound **1**. The same may not be true in the molybdenum system. It is worth noting in this respect that when the more basic and less sterically demanding dmpm ligand was employed, $MoI_2(CO)(dmpm)_2$ was obtained, and this was found to be fairly stable in refluxing toluene.³

The room-temperature reaction of $W_2I_4(CO)_8$

* $W_2Cl_4(PMe_3)_4$ has the $\delta \rightarrow \delta^*$ absorption at 657 nm, *ca* 80 nm red-shifted with respect to the same band of $Mo_2Cl_4(PMe_3)_4$.¹⁰ Since $Mo_2I_4(dppm)_2$ has the $\delta \rightarrow \delta^*$ maximum at 707 nm,² the hypothetical $W_2I_4(dppm)_2$ compound is expected to have the same band at a higher wavelength, around 800 nm.

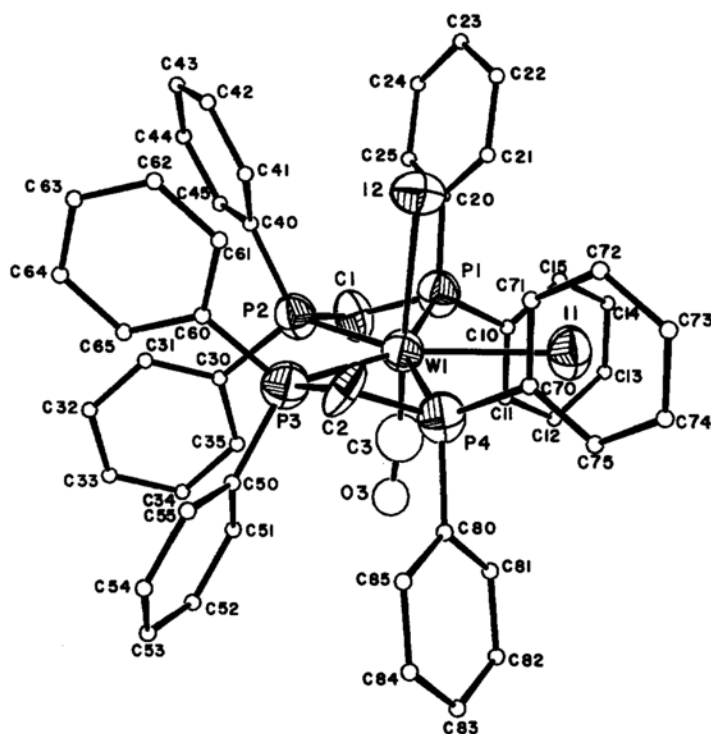


Fig. 1. ORTEP view of the molecule of compound 1 which lies in a general position. Atoms I(3), C(4) and O(4) have been omitted for the sake of clarity. For the same reason, the phenyl carbon atoms have been drawn with arbitrary radii.

with PMe_3 produced a solution containing several products, as judged from the complexity of the IR spectrum. Some of the bands could presumably be assigned to $WI_2(CO)_3(PMe_3)_2$ [the room-temperature interaction of $W_2I_4(CO)_8$ with PPh_3 was reported⁵ to afford the tricarbonyl derivative, $WI_2(CO)_3(PPh_3)_2$]. After prolonged reflux with simultaneous UV irradiation, $WI_2(CO)_2(PMe_3)_3$ (**2**) was the major product, isolated in *ca* 33% yield with respect to tungsten (49.5% with respect to PMe_3). The fate of the rest of the tungsten is unknown, although small amounts of a more soluble material, having an IR band at 1731 cm^{-1} , were detected by IR spectroscopy; the position of the IR band suggests that this compound may be a monocarbonyl derivative of tungsten(II). Again, visible absorption bands in the 600–900-nm region were not detected in the final solution, which means that tungsten(II) dimers with a quadruple bond between the metals did not form. This is again in contrast with the results of the same reaction on molybdenum systems.^{1,4}

The formation of tungsten–tungsten quadruple bonds by decarbonylation of tungsten(II) carbonyl derivatives proves then to be a difficult, if not impossible, reaction, contrary to what was found for the analogous molybdenum systems. One factor

contributing to this might be the higher stability of the tungsten(II) carbonyls with respect to those of molybdenum(II), as suggested by higher W–CO bond energies, at least for M(0) derivatives.¹⁵ Also, the molybdenum–molybdenum quadruple bond is generally less reactive than the same bond between tungsten(II) ions, and thus more likely to remain intact once formed. Both these factors should cause the decarbonylation of tungsten(II) carbonyls to be more difficult and, in turn, the reaction of $W_2X_4L_4$ (W^4 –W) systems with CO to be easier. A few reactions of $W_2Cl_4(PR_3)_4$ systems with CO have actually been studied and reported to be more facile than those of the corresponding molybdenum(II) dimers.¹⁶

Acknowledgement—This work was supported by the National Science Foundation.

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