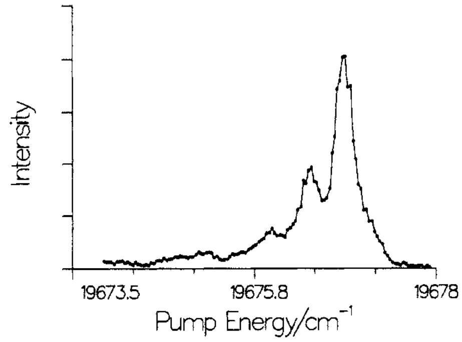

Figure 1. Excitation spectrum of the $XeCl_2$, B ← X, 10 ← 0 transition observed by detecting $Cl_2(B,v=8)$. The corresponding Cl_2, B ← X, 10 ← 0 transition occurs 9.5 cm^{-1} to the red of this peak.

molecule has never been isolated or even unambiguously identified.

The structures and bond energies of the $HeCl_2$, $NeCl_2$, and $ArCl_2$ van der Waals molecules are well determined and show no signs of incipient chemical bonding in either the ground electronic state or the B excited electronic state that is reached upon excitation with green light.[5] In previous attempts to study $XeCl_2$ by laser-excited fluorescence, the B ← X transition could not be observed. Since the B state of Cl_2 is near the dissociation energy of the ground-state Cl_2 potential, it seemed possible that excitation of the $XeCl_2$ van der Waals ground state led to a chemical reaction rather than a detectable fluorescence signal. Indeed, such dynamics are observed in the vicinity of the $^1\Pi_u$ state.[6]

In the present study, the two-laser pump–probe method, described previously,[7] was used to observe the $XeCl_2$ B ← X spectrum and the Cl_2 products of vibrational predissociation. Briefly, ground-state $XeCl_2$ van der Waals clusters are formed in a free jet expansion of a 1700-kPa 2% Xe/helium mixture seeded with 10 Pa of Cl_2. The first laser "pumps" the cluster into an electronically and vibrationally excited state associated with the B state of free Cl_2. Vibrational energy is then transferred from the Cl_2 stretch into the van der Waals modes, and dissociation occurs. The second laser "probes" the production of free Cl_2 after dissociation via the E ← B electronic transition. Fluorescence from the Cl_2 E state gives the detected signal. Figure 1 shows a $XeCl_2$ excitation spectrum in which the probe laser is set to detect $Cl_2(B,v=8)$ while the pump laser is scanned across the $XeCl_2$ B, $v = 10$ ← X excitation. The signal-to-noise ratio for this spectrum is lower than that achieved for other rare gas–Cl_2 clusters. It is not presently known if this is due to lower production of the $XeCl_2$ ground state in the supersonic expansion or to other dynamics competing with vibrational predissociation of the electronic excited state.

A reasonable fit to the spectrum in Figure 1 can be made by assuming that the complex is T-shaped in both the X and B states, as for $HeCl_2$, $NeCl_2$, and $ArCl_2$.[5] The structure in the spectrum is mainly due to near-prolate K-type transitions that mainly involve rotation of the Cl_2 constituent about the Xe–Cl_2 axis. This assignment is further supported by parity selectivity in the dissociation process.[7] If the probe laser is positioned to detect the production of an even rotational state of the Cl_2 fragments, then only even values of the prolate K quantum number are observed in the excitation spectrum. The resolution of the spectrum is insufficient to resolve rotations which would determine the Xe–Cl bond lengths. From the bandwidths we can establish a lower limit for the excited-state lifetime of 50 ps. When probe spectra are used as described previously,[8] the bond energies for the Xe–Cl_2 van der Waals attraction are determined to be 3.69 ± 0.01 kJ/mol in the ground electronic state and 3.33 ± 0.01 kJ/mol in the excited electronic state. These values are 1.5 times greater than the bond energies in the $ArCl_2$ complex[9] and are as expected for van der Waals bonding; no signs of the formation of a chemical bond between the xenon and chlorines is observed.

In summary, two electronic states of the van der Waals isomer of $XeCl_2$ have been observed. Even with electronic and vibrational excitation to within 1.7 kJ of the Cl_2 dissociation energy, the van der Waals isomer is stable for at least 50 ps. If the linear Cl–Xe–Cl molecule is as stable as predicted, then there must be a large barrier in the bending mode that separates it from the van der Waals isomer.

Acknowledgment. This research was supported by the National Science Foundation.

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New Radical Chain Reaction of *S*-Alkoxycarbonyl Dithiocarbonates: A Useful Source of Alkyl Radicals from Alcohols

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The past few years have witnessed a dramatic growth in the development and use of radical reactions in organic synthesis.[1] One important requisite for radical-based methodology is the availability of a convenient source of carbon radicals from various functional groups. In this communication, we report a new method for generating alkyl radicals from alcohols through decarboxylation of the corresponding alkoxycarbonyl radical. This novel procedure follows from our recent work[2] on the radical chemistry of dithiocarbonates and xanthates in particular.

Alkoxycarbonyl radicals (ROCO) have seldom found use as precursors of the corresponding alkyl radicals (R$^\bullet$), mainly because release of carbon dioxide from these species is relatively slow in comparison with other possible competing processes usually inherent to the method of generation.[3,4] Limited kinetic studies[5] on *tert*-butoxycarbonyl radicals have yielded a rate constant of 10^5–10^6 s^{-1} at 60 °C for the unimolecular decarboxylation step. Ethoxycarbonyl radicals, which produce the higher energy ethyl radicals, are reported to extrude carbon dioxide much more

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(1) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Curran, D. P. *Synthesis* **1988**, 417 and 489. (c) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (d) Neumann, W. P. *Synthesis* **1987**, 665. (e) Hart, D. J. *Science* **1984**, *223*, 883.

(2) (a) Delduc, P.; Tailhan, C.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, 308. (b) Mestre, F.; Tailhan, C.; Zard, S. Z. *Heterocycles* **1989**, *28*, 171. (c) Forbes, J. E.; Zard, S. Z. *Tetrahedron Lett.* **1989**, *30*, 4367. (d) See also: Barton, D. H. R.; George, M. V.; Tomoeda, M. *J. Chem. Soc.* **1962**, 1967.

(3) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328. These authors propose in one of their schemes that the alkoxycarbonyl radical could also extrude carbon monoxide to give an alkoxy radical. This, however, is highly unlikely in view of earlier kinetic studies which indicate that the reverse process is more favored (see, for example: Lissi, E. A.; Scaiano, J. C.; Villa, A. E. *J. Chem. Soc., Chem. Commun.* 1971, 457). We thank a referee for raising this point.

(4) (a) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Chem. Commun.* **1984**, 774; (b) *Tetrahedron Lett.* **1985**, *26*, 757; (c) *J. Chem. Soc., Perkin Trans. 1* **1986**, 1603. (d) Crich, D.; Fortt, S. M. *Synthesis* **1987**, 35.

(5) (a) Griller, D.; Roberts, B. P. *J. Chem. Soc., Chem. Commun* **1971**, 1035; (b) *J. Chem. Soc., Perkin Trans. 2* **1972**, 747. (c) Ingold, K. U.; Maillard, B.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 970. (d) Rüegge, R.; Fischer, H. *Int. J. Chem. Kinet.* **1986**, *18*, 145. (e) Beckwith, A. L. J.; Bowry, V.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632.

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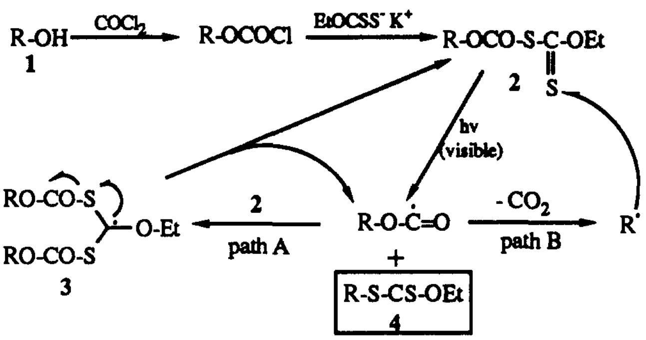
Scheme I



slowly.[5a] Indeed the slow loss of carbon dioxide from alkoxycarbonyl radicals allows their ready capture with appropriate olefins in an intra- or even intermolecular fashion to produce lactones or esters,[6] although in the latter case yields tend to be low.

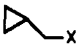
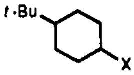
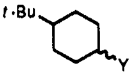
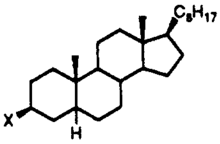
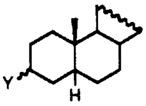
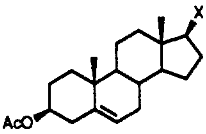
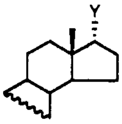
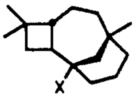
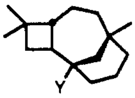
If alkoxycarbonyl radicals are to be used as useful precursors of the corresponding alkyl radicals, they must be generated in such a way as to give them sufficient lifetime in the medium to allow them to extrude carbon dioxide. As outlined in Scheme I, the system based on *S*-alkoxycarbonyl xanthates **2** fulfills this crucial condition in a very simple way. Surprisingly enough, these easily accessible compounds have hardly received any attention, even though the symmetrical diethyl derivative (**2**, R = Et) was first prepared at the beginning of the century.[7]

Thus, by analogy with *S*-acyl xanthates,[2] which give an acyl radical on irradiation with visible light, *S*-alkoxycarbonyl xanthates **2** should lead to the corresponding alkoxycarbonyl radical. In the same way, the reaction of this species with its precursor **2** (path A) is *reversible and degenerate* since the resulting *symmetrical* intermediate **3** can only collapse to give back the same alkoxycarbonyl radical and **2** (fragmentation by rupture of the strong O–Et bond is highly unlikely). *This reaction does not therefore compete with the expulsion of carbon dioxide* (path B), in sharp contrast to previous processes based on stannane chemistry[3] or on thiohydroxamate esters[4] where such a competition restricts their synthetic utility to examples involving an especially rapid decarboxylation step, as is the case when a relatively stabilized alkyl radical (e.g., tertiary) is produced.

In its simplest form, the process delineated in Scheme I would convert an alcohol **1** into the corresponding *S*-xanthate **4** through a radical chain mechanism, the overall result being the replacement of a carbon–oxygen with a carbon–sulfur bond. This conception was easily and successfully tested on a number of tertiary, secondary, and even primary aliphatic and alicyclic alcohols as illustrated by the examples compiled in Table I. No reaction takes place in the absence of light.

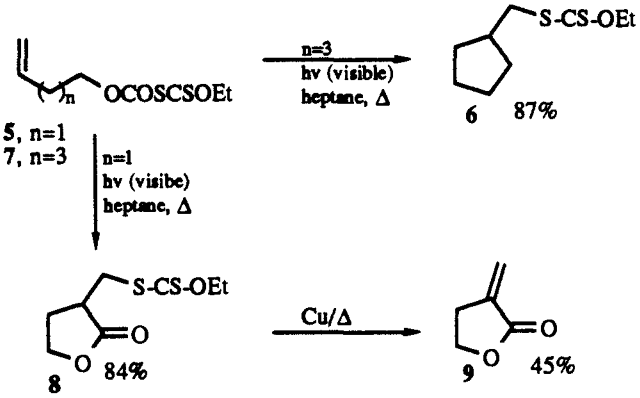
The transformation of the cyclopropylmethyl derivative (entry 4) into *S*-3-butenyl *O*-ethyl xanthate may be construed as strong evidence that the process is indeed a radical chain and not an ionic or S_Ni type decarboxylate rearrangement. The well-known,[8] very fast rearrangement of the cyclopropylmethyl radical into 3-butenyl radical occurs before transfer of the xanthate group. Furthermore, if the starting alcohol contains a suitably located double bond, both the alkoxycarbonyl and the ensuing alkyl radical may be captured. Thus, starting from 5-hexen-1-ol, the corresponding derivative **7** (*n* = 3) was smoothly converted on irradiation with visible light in refluxing heptane (0.01 M) into *S*-cyclopentylmethyl *O*-ethyl xanthate (**6**)[9] in 87% yield (Scheme II). Clearly in this case, cyclization of the first formed (5-hexenyloxy)carbonyl radical to give a seven-membered-ring lactone is slower than decarboxylation. The same compound was obtained in comparable yield when heptane was replaced by the lower boiling cyclohexane.[10] In contrast, irradiation under similar conditions of **5**

Table I. Decarboxylative Rearrangement of *S*-Alkoxycarbonyl Dithiocarbonates[a]

entry	*S*-alkoxycarbonyl dithiocarbonate	time, h	product	yield, %
1	EtX	2.5	EtY	59
2	$C_{16}H_{33}X$	2.0	$C_{16}H_{33}Y$	73
3	Me_2CHCH_2X	2.5	Me_2CHCH_2Y	61
4		4.5		59
5		1.0		52[b]
6		1.0		71[c]
7		2.5		83
8		1.25		92

[a] X = OCOSCSOEt; Y = SCSOEt; unless otherwise stated, reactions were conducted in refluxing heptane with a 500-W tungsten filament lamp for irradiation. [b] Obtained as a 2:1 cis–trans mixture as determined by NMR. [c] Reaction conducted in boiling toluene; the product consisted of a 4:1 mixture of α and β isomers.

Scheme II



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(6) (a) Urry, W. H.; Huyser, E. S. *J. Am. Chem. Soc.* **1953**, *75*, 4876–4877. (b) Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1986**, *27*, 641–644; **1988**, *29*, 2581–2584. (c) Crich, D.; Fortt, S. M. *Ibid.* **1987**, *28*, 2895–2898.

(7) (a) Holmberg, B. *J. Prakt. Chem.* [*2*] **1905**, *71*, 264. (b) Sayre, R. *J. Am. Chem. Soc.* **1952**, *74*, 3647. (c) Carpino, L. A.; Terry, P. H.; Crowley, P. J. *J. Org. Chem.* **1961**, *26*, 4336. (d) Palominos, M. A.; Santos, J. G.; Valderrama, J. A.; Vega, J. C. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2641. (e) Castro, E. A.; Meneses, B.; Santos, J. G.; Vega, J. C. *J. Org. Chem.* **1985**, *50*, 1863. (f) Barany, G.; Schroll, A. L.; Mott, A. W.; Halsrud, D. A. *Ibid.* **1983**, *48*, 4750. (g) Barany, G.; Mott, A. W. *Ibid.* **1984**, *49*, 1043. Note: these compounds are indexed by Chemical Abstracts as esters of thiodicarbonic acid.

(8) (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (b) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Seralio, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734. (c) See also ref 5e.

(9) Ring closure of the 5-hexenyl radical into the cyclopentylmethyl radical is perhaps one of the best known of radical cyclizations: (a) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739. (b) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925 and references there cited.

(10) The possibility of obtaining cleanly, at this comparatively low temperature, a *primary radical* from a primary alcohol through its alkoxycarbonyl xanthate derivative contrasts very favorably with previous work involving alkoxycarbonyl radicals (refs 3 and 4) and highlights the advantages of this approach. Moreover, access to primary radicals by treatment of thiocarbonyl derivatives of primary alcohols with tributylstannane is rather difficult in general; see: (a) Barton, D. H. R.; Motherwell, W. B.; Stange, A. S. *Synthesis* **1982**, 743. (b) Tulshian, D. B.; Fraser-Reid, B. *Tetrahedron Lett.* **1980**, *21*, 4549.

(n = 1) obtained from 3-buten-1-ol furnished the corresponding lactone **8** in excellent yield (84%). This time, the 5-exo cyclization of the intermediate (3-butenyloxy)carbonyl radical is faster than decarboxylation. Heating **8** with copper powder under vacuum caused the elimination of the xanthate group[2a] and provided the known *exo*-methylene lactone **9** (also called tulipalin A) in 45% yield.

Apart from providing incontrovertible evidence as to the radical nature of the intermediates, the last two experiments underscore the flexibility and synthetic potential of this novel reaction as a mild generator of carbon-centered radicals from alcohols.

Acknowledgment. We would like to thank Drs. J. Boivin, J.-Y. Lallemand, and D. Lefort for friendly and stimulating discussions. One of us (J.E.F.) acknowledges with gratitude the receipt of a Royal Society Fellowship.

Unprecedented Bonding Mode in $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4W(CO)_5$

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We have recently described the preparation of complexes of the type $(R_3P)(OC)_4OsM(CO)_5$ (M = Cr, Mo, W) in which the 18-electron compound $Os(CO)_4(PR_3)$ acts as a ligand to the group 6 metal atom via an unbridged, donor-acceptor metal-metal bond.[1] In the preparation of one of these derivatives, namely, $(L)(OC)_4OsW(CO)_5$ (L = $P(OCH_2)_3CMe$), low yields of a second compound were obtained, the ^{13}C NMR spectrum of which indicated it to be $(L)(OC)_4OsOs(CO)_3(L)W(CO)_5$ (**2**) with two unbridged, dative metal-metal bonds.[2] This prompted an investigation into the rational synthesis of such compounds, and here we report the synthesis and structure of $(OC)_3(L)_2OsOs(CO)_4W(CO)_5$ (**1**), an isomer of **2**. The crystal structure confirms the presence of unbridged, dative metal-metal bonds in tandem in **1**. Such a bonding mode has, to our knowledge, not been previously observed.

A hexane/THF solution of $(L)(OC)_4OsW(CO)_5$ and $Os(CO)_4(L)$ (in a molar ratio of 0.67:1) was heated under vacuum at 90 °C for 6.4 days, during which time a yellow solid precipitated. The yellow solid was chromatographed (alumina, CH_2Cl_2/hexane, 1/2, as eluant) and gave a yellow band from which **1** was obtained (22% yield) upon recrystallization as yellow, air-stable crystals.[3] The structure[4] of **1** (Figure 1) reveals an approximately linear arrangement of the Os_2W atoms; each of the metal-metal bonds is unbridged. An electron count for each metal atom indicates that both metal-metal bonds should be regarded as dative bonds in order for each metal atom to achieve an 18-electron configuration. This is shown below (the eclipsed form is drawn for convenience).

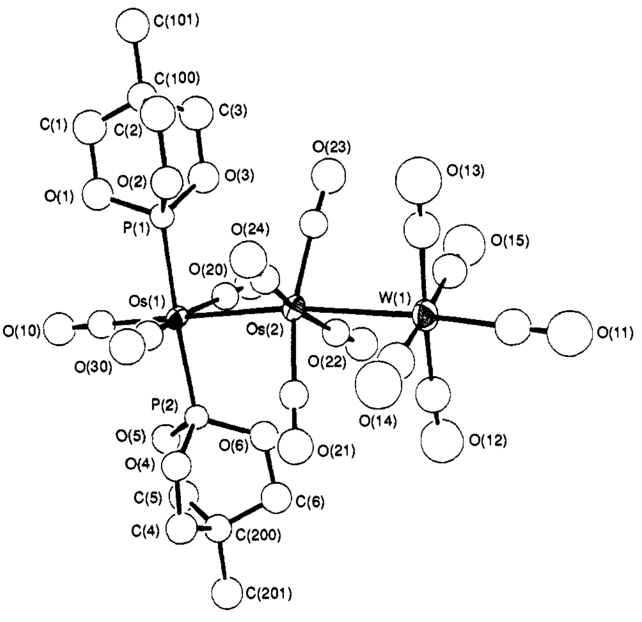
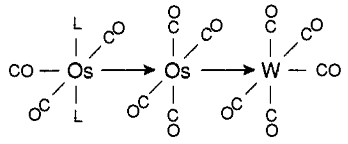


Figure 1. Molecular structure of $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4W(CO)_5$ (**1**).



I

The complex is remarkably stable (note that it was prepared in a reaction at 90 °C that took several days to go to completion). It appears more thermally stable than any of the $(R_3P)(OC)_4OsW(CO)_5$ complexes[1] that have a single dative metal-metal bond. This extra stability may be the result of greater charge separation when two dative metal-metal bonds are linked as in **1** (i.e., $(\delta+)Os \rightarrow Os \rightarrow W(\delta-)$). The Os-W bond length in **1** at 3.039 (1) Å is somewhat shorter than that in $(Me_3P)(OC)_4OsW(CO)_5$ (3.0756 (5) Å)[1] and in $(OC)_3(Me_3P)_2OsW(CO)_5$ (3.1417 (6) Å).[5] The Os-Os distance in **1** (2.940 (1) Å) is comparable to the dative Os-Os bond distances found in the three independent molecules in the unit cell of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$ (2.916 (2), 2.927 (2), 2.931 (2) Å)[6] and the covalent Os-Os bond lengths in $Os_3(CO)_{12}(SiCl_3)_2$ (2.9120 (1) Å)[7] and $Os_3(CO)_{12}(I)_2$ (2.935 (2) Å).[8] The Os(1)-Os(2)-W angle (172.07 (4)°) in **1** is virtually identical with the P-Os-W angle in $(Me_3P)(OC)_4OsW(CO)_5$ (171.31 (4)°).[1]

The ^{13}C NMR spectrum of **1** in CH_2Cl_2/CD_2Cl_2 clearly shows that the solid-state structure is maintained in solution.[3] The spectrum also indicates that **1** should be formulated as shown and not $(OC)_3(L)_2Os \rightarrow W(CO)_4 \leftarrow Os(CO)_5$. In contrast to **2**,[2] $(L)(OC)_4OsW(CO)_5$,[1] and $(OC)_3(Me_3P)_2OsW(CO)_5$,[5] there is no evidence for a second isomer in solution. The resonance at δ 165.6 in the spectrum of **1** is attributed to C(10) (Figure 1).

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(1) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. *Organometallics* **1989**, *8*, 1030.

(2) Isolated yield: 13% (after chromatography). IR: ν(CO) (CH_2Cl_2) 2126 (w), 2114 (w), 2051 (s), 2041 (s), 2008 (m, sh), 1973 (m, sh), 1957 (s), 1904 (s), 1844 (m) cm^{-1}. ^{13}C NMR (CD_2Cl_2/CH_2Cl_2, 1/4): major isomer (L trans to the Os-Os bond), δ 206.4 (1), 203.8 (4, $J_{^{183}W-C}$ = 123.9 Hz), 195.8 (2, d, J_{P-C} = 19.2 Hz), 192.4 (1, d, J_{P-C} = 121.4 Hz), 179.9 (4, d, J_{P-C} = 6.7 Hz); minor isomer (L cis to Os-Os bond), δ 203.9 (4), 195.4 (2, d, J_{P-C} = 20.2 Hz), 180.2 (2, d, J_{P-C} = 18.4 Hz), signals of intensity 1 of the minor isomer were not observed. Anal. Calcd for $C_{22}H_{18}Os_2WO_{18}P_2$: C, 22.08; H, 1.52. Found: C, 21.86; H, 1.53.

(3) IR: ν(CO) (CH_2Cl_2) 2101 (w), 2059 (s), 2022 (vs), 1977 (vs), 1902 (s), 1856 (m) cm^{-1}. ^{13}C NMR (CH_2Cl_2/CD_2Cl_2, 4/1): δ 206.4 (1, $J_{^{183}W-C}$ = 177 Hz), 204.1 (4, $J_{^{183}W-C}$ = 125.1 Hz), 193.3 (4), 183.2 (2, t, J_{P-C} = 16.1 Hz), 165.6 (1, t, J_{P-C} = 11.1 Hz). ^{31}P NMR (CH_2Cl_2/CD_2Cl_2,4/1): δ 78.1. Anal. Calcd for $C_{22}H_{18}Os_2WO_{18}P_2$: C, 22.08; H, 1.52. Found: C, 22.33; H, 1.54.

(4) X-ray diffraction data for $(OC)_3[MeC(CH_2O)_3P]_2OsOs(CO)_4W(CO)_5$: M_r = 1196.6; monoclinic; space group $P2_1/c$; a = 16.291 (3) Å, b = 11.415 (3) Å, c = 17.371 (3) Å, β = 91.40 (2)°; V = 3229.4 Å^3; Z = 4; D_{calcd} = 2.461 g cm^{-3}; μ = 116.6 cm^{-1} (an absorption correction based on ψ scans was applied); diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator ($\lambda(K\alpha_1)$ = 0.709 30 Å); $4° \leq 2\theta \leq 48°$; reflections = 2700 with $I_o > 2.5\sigma(I_o)$; (number of variables = 176) R_F = 0.043, R_{wF} = 0.048. Residual peaks of up to 2.0 (1) e/Å^3 occur 0.9-1.0 Å from Os and W atoms. Attempts to develop an improved model for the structure are in progress.

(5) Davis, H. B.; Einstein, F. W. B.; Martin, L. R.; Pomeroy, R. K. To be submitted for publication.

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