and consequently longer triplet lifetimes (greater energy gap between the triplet- and ground-state surfaces) and larger values of k_q. The observed correlation between the flash and steady-state data is indeed gratifying.

However, it is now clear that the situation is much more complicated. From steady-state experiments, we know that alkenes quench the photorearrangement of **2** through formation of [2 + 2] cycloadducts, suggesting a common precursor to these two reactions.[11] Amines such as triethylamine and 1,4-diazabicyclo[2.2.2]octane (Dabco) also efficiently quench the photorearrangement, with $k_q\tau_T$ values of 6.7 and 25.7 in isopropyl alcohol (IPA), respectively; presumably this occurs by photoinduced electron transfer leading in part to enone–amine adducts.[12] However, the 280-nm absorptions of **2** and **4** were not affected by up to 1.6 M cyclohexene and 1.0 M 1,1-dimethoxyethylene (DME) while DME reduces the rise time of the NA triplet absorption on excitation of **2** and **4**, as shown in Figure 1. Studies of quenching of these 280-nm transients by amines are problematic, because of the appearance of a long-lived (microsecond lifetime) amine-dependent transient absorption at 280 nm that rapidly obscures the decay of the fast transient. Using Dabco at concentrations up to 0.06 M in IPA and 0.02 M in CH_3CN, where the fast transient decay of **1**, **2**, and **4** is still measurable, we observed no effect on the enone transient lifetimes, within the precision of our measurements, which is estimated at ±10% from repeated flashes and alternative methods of analysis of the decay kinetics.[13] Finally, 1,3-cyclohexadiene (CHD) up to 0.012 M did not quench the 280-nm transient decay of **2** in cyclohexane, although a long-lived transient absorption ascribed to CHD triplets was observed at 295 nm.[14]

Despite the agreement between the directly measured lifetimes of the 280-nm enone transients and the extrapolated lifetimes from NA quenching studies, we are forced to conclude that at least in the cases of **2** and **4** the 280-nm transient is not the species that (a) is quenched by NA and CHD, (b) reacts with alkenes and Dabco, and (c) leads to photorearrangement products. These latter processes appear to proceed via a phantom triplet species that has yet to be detected directly in flash studies but whose properties are consistent with that of a relaxed twisted triplet state. The identity of the 280-nm enone transient in these cases is unclear,[15] but it is apparently not directly involved in the formation of any observed photochemical reaction product.[16] In the cases of testosterone (**5**) and enone **6** (which is constrained from rearrangement),[17] it is likely that these two species merge, since the 280-nm transient can be directly quenched in a linear fashion by dienes. Furthermore, other steady-state and flash data suggest that photodimerization of enones **1** and **2** as well as photoreduction in IPA entirely bypass these transients and occur via yet another much shorter-lived triplet excited state.[4,10,12]

Experiments in progress will hopefully clarify this unexpectedly complex situation.

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Registry No. 1, 930-68-7; **2**, 1073-13-8; **3**, 13395-71-6; **4**, 6606-34-4; **5**, 58-22-0; **6**, 73013-93-1; **7**, 826-56-2.

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[11] Schuster, D. I.; Greenberg, M. M.; Nuñez, I. M.; Tucker, P. C. *J. Org. Chem.* **1983**, *48*, 2615.

[12] For kinetic studies of the effects of triethylamine on the photochemistry of **1**, see: Pienta, N. J.; McKimmey, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 5501.

[13] Preliminary data using octalone **7** suggests that Dabco quenches growth of NA triplet absorption.

[14] Similar absorption was seen on sensitization of CHD by thioxanthone.

[15] As noted by one of the referees, the agreement between the measured lifetime of the 280-nm transient and the "phantom triplet" discussed in the text for so many cases (see Table I) cannot be coincidental. This suggests that there must be a kinetic relationship between the two species. One plausible suggestion is that the 280-nm species is the precursor of the quenchable triplet, forming it irreversibly, with subsequent steps being fast on this time scale. However, the fact that the 280-nm transient of **2** is not quenchable by 1,3-cyclohexadiene (E_T = 52 kcal/mol) would appear to be inconsistent with such a scheme. Another suggestion is that the 280-nm species is a monomeric triplet, while the quenchable "phantom" triplet is an excimeric species.[12] The following results make this proposal unlikely. First, the rate of decay and optical density of the 280-nm species of **1** and **2** are not affected by either enone concentration or solvent viscosity. Second, our results suggest that NA and DME are reacting with the same species. If this is indeed a triplet excimer in equilibrium with the monomer, as proposed by Pienta and McKimmey,[12] then the lifetime of the 280-nm species should decrease with increasing concentrations of DME, which was not observed (see Figure 1). The dependence of the lifetime of both intermediates on molecular structure suggests that both species have similar (twisted) geometries.

[16] Pienta has come to a similar conclusion based on his studies of enones with amines reported in the preceding communication.

[17] Schuster, D. I.; Hussain, S. *J. Am. Chem. Soc.* **1980**, *102*, 409.

18-Electron Complexes as Ligands. Synthesis, Structure, and Stereochemical Nonrigidity of $(Me_3P)(OC)_4OsW(CO)_5$

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We have recently described the synthesis and crystal structure of $(OC)_5OsOs(CO)_3(GeCl_3)(Cl)$, a compound in which the 18-electron complex, $Os(CO)_5$, acts as a donor ligand to the second osmium atom.[1] We now report the preparation of $(Me_3P)(OC)_4OsW(CO)_5$, the structure of which reveals it to contain an unbridged donor–acceptor bond between different transition-metal atoms. The compound also exhibits stereochemical nonrigidity in solution, which is unusual for binuclear complexes in which the metal atoms are six-coordinate with monodentate ligands.

The reaction of $W(CO)_5(THF)$ with $Os(CO)_4(PMe_3)$[2] in hexane affords $(Me_3P)(OC)_4OsW(CO)_5$ (**1**) within a few minutes; the compound was isolated by chromatography (Florisil, hexane-CH_2Cl_2 eluant) in 55% yield as air-stable, pale-yellow crystals.[3] A single-crystal X-ray diffraction study[4] shows that the 18-electron compound, $Os(CO)_4(PMe_3)$, acts as a donor ligand to the $W(CO)_5$ unit via an unbridged osmium–tungsten donor–acceptor bond (Figure 1). The strong donor ligand trimethylphosphine is trans to this bond. The Os–W bond length found for **1** (3.0756 (5) Å) is somewhat longer than unbridged Os–W bonds observed in metal clusters (range 2.663 (3)–3.066 (3) Å);[5] the bond is also longer than that determined in $Re_2(CO)_{10}$ (3.041 (1) Å).[6] The inward leaning of the radial carbonyls on osmium

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[1] Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. *J. Chem. Soc., Chem. Commun.* **1983**, 854.

[2] Details of the preparation of $Os(CO)_4(PMe_3)$ will be submitted shortly. See, however: Martin, L. R.; Einstein, F. W. B.; Pomeroy, R. K. *Inorg. Chem.* **1983**, *22*, 51.

[3] Compound **1**: IR (CH_2Cl_2) ν (CO) 2093 (w), 2040 (m), 2008.5 (s), 1911.5 (s), 1877.5 (m) cm^{-1}, MS, *m/e* 703 (w) (M^+). Anal. Calcd for $C_{12}H_9O_9POsW$: C, 20.53; H, 1.29. Found: C, 20.50; H, 1.21.

[4] Crystal data for **1**, $C_{12}H_9O_9POsW$: M = 702.2; monoclinic; space group $P2_1/n$; a = 8.832 (1) Å, b = 16.241 (2) Å, c = 12.988 (2) Å; β = 101.99 (1)°; V = 1822.35 $Å^3$, D_c = 2.560 g cm^{-3}; Z = 4; μ(Mo Kα) = 135.42 cm^{-1}. Structure solved by conventional methods; final agreement factors (2189 observed reflections) were R_f = 0.019 and R_w = 0.023.

[5] Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161; 843. Churchill, M. R.; Bueno, C.; Wasserman, H. J. *Ibid.* **1982**, *21*, 640. Busetto, L.; Green, M.; Hessner, B.; Howard, J. A. K.; Jeffrey, J. C.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 519. Park, T. J.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *J. Am. Chem. Soc.* **1983**, *105*, 6182.

[6] Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

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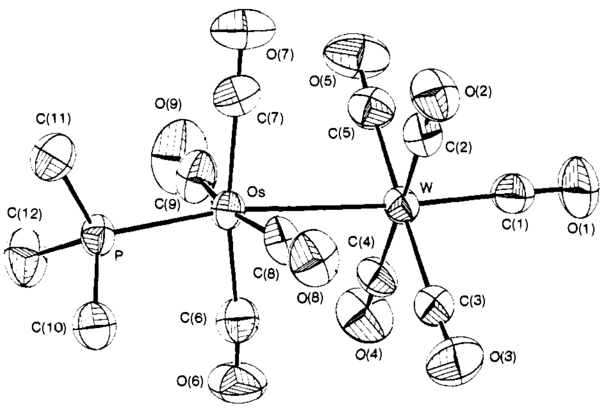
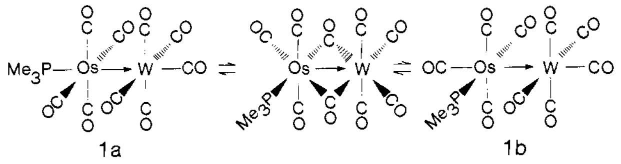


Figure 1. ORTEP diagram for $(Me_3P)(OC)_4OsW(CO)_5$. Selected distances (Å), Os–W = 3.0756 (5), Os–P = 2.359 (2), Os–C range 1.941 (7)–1.954 (8), W–C(1) = 1.964 (8), W–C(equatorial) range 2.021 (7)–2.045 (8), and angles (deg) W–Os–P = 171.31 (4); W–Os–C range 80.2 (2)–89.1 (2); Os–W–C(equatorial) 84.7 (2)–93.9 (2).

Scheme I



(C(6)–Os–C(7) = 169.0 (3)°, C(8)–Os–C(9) = 167.9 (3)°) has its counterpart in decacarbonyldirhenium.[6]

The strongest signals in the ^{13}C NMR spectrum of **1** (CH_2Cl_2/CD_2Cl_2 solution) were consistent with the solid-state structure (**1a**). However, minor peaks were observed, the intensity of which did not change even after further chromatography and recrystallization of the sample. The ^1H NMR spectrum of **1** in CD_2Cl_2 similarly showed two methyl doublets centered at δ 2.01 ($J_{\mathrm{P-C}}$ = 10.5 Hz) and 1.92 ($J_{\mathrm{P-C}}$ = 10.3 Hz) in the ratio 7.1:1. The minor signals in each case were assigned to the isomer of **1** that had the trimethylphosphine ligand in a radial position on osmium, i.e., **1b** (Scheme I, eclipsed forms drawn for convenience). This conclusion was confirmed by the solution ^{13}C NMR spectrum of **1** prepared from $Os(CO)_4(PMe_3)$ that had been enriched in ^{13}CO.[7] Previously unobserved signals were entirely consistent with the presence of ~14% of the **b** form of **1**. Of special interest was that the ^{13}C labeled carbonyls had become scrambled between the osmium *and the tungsten atoms*.[8]

Evidence that the two isomers were in dynamic equilibium was provided by a spin saturation transfer NMR experiment. Saturation of the signal at 2.03 ppm (assigned to **1a**) in the ^1H NMR of **1** in CD_2Cl_2 caused transfer to the signal at 1.93 ppm (assigned to **1b**). A similar experiment was carried out with $Os(CO)_4(PMe_3)$ added to the solution. There was no transfer to the doublet due to the added component, nor was the transfer to the signal due to **1b** affected (Figure 2). This result indicated that dissociation of **1** to give $Os(CO)_4(PMe_3)$ and $W(CO)_5$ was not involved in the isomerization. Furthermore, **1** did not exchange with ^{13}CO when it was stirred in CH_2Cl_2 under 1 atm of this reagent nor did it react, in solution at room temperature, with PMe_2Ph.[9]

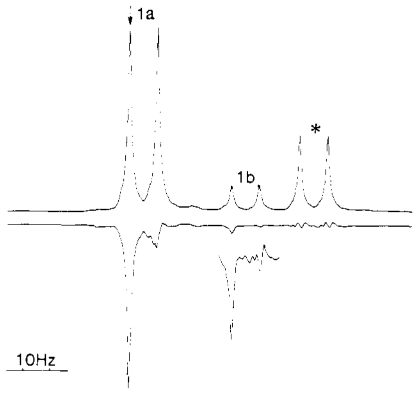


Figure 2. Spin saturation transfer experiment on $(Me_3P)(OC)_4OsW(CO)_5$. Irradiation of the lowest field ^1H NMR resonance due to one isomer (**1a**) resulted in transfer to the corresponding signal of the second isomer (**1b**). No transfer occurred to the signals due to added $Os(CO)_4(PMe_3)$ (*).

A mechanism that accounts for the isomerization and the nondissociative carbonyl migration from osmium to tungsten is shown in Scheme I (it is assumed that there is rotation about the Os–W bond in the unbridged forms). The suggested mechanism implies that the isomerization occurs at the same rate as carbonyl exchange, which has not, as yet, been established.

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Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles (6 pages). Ordering information is given on any current masthead page.

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[7] The ^{13}CO enrichment was achieved by the mild ultraviolet irradiation of $Os(CO)_4(PMe_3)$ in hexane under ca. 1.5 atm of ^{13}CO.

[8] The complete $^{13}C\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2/CH_2Cl_2 (1:5): **1a**, δ 204.6 (1, d, $J_{\mathrm{P-C}}$ = 2.2, $J_{^{183}\mathrm{W-C}}$ = 179.1 Hz), 202.8 (4, s, $J_{^{183}\mathrm{W-C}}$ = 124.9 Hz), 186.7 (4, d, $J_{\mathrm{P-C}}$ = 3.0, $J_{^{187}\mathrm{Os-C}}$ = ~92 Hz), 23.2 ($J_{\mathrm{P-C}}$ = 37.1 Hz); **1b**, 202.9 (1, s), 202.5 (4, s, $J_{^{183}\mathrm{W-C}}$ = 125.2), 188.3 (2, d, $J_{\mathrm{P-C}}$ = 13.2 Hz), 176.0 (1, d, $J_{\mathrm{P-C}}$ = 71.1 Hz), 170.3 (1, d, $J_{\mathrm{P-C}}$ = 8.9 Hz), 20.8 ppm (d, $J_{\mathrm{P-C}}$ = 37.7 Hz). The first number in parenthesis for the carbonyl resonances represents the approximate, overall intensity of the signal relative to the other carbonyl signals of the isomer.

[9] Solutions of **1** did show some decomposition after 24 h; $W(CO)_6$ was identified as one of the decomposition products. The amount of $W(CO)_6$ did not appear to increase when solutions of **1** were stirred under CO (65 atm) for 24 h. Rapid decomposition in solution above 60 °C precluded NMR line-broadening studies on **1**.

Novel and Stereospecific Imide Synthesis

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The past 10 years have witnessed an increased awareness of the importance of transition-metal complexes as reagents, and as catalysts, in heterocyclic synthesis.[1] One facet of this subject involves the utilization of strained-ring heterocycles as precursors to other heterocyclic systems via appropriate ring opening and closing reactions.[2] For example, azirines are convertible to pyrazines, isoxazoles, pyrazoles, or pyrroles on exposure to molybdenum and other group 6 metal carbonyls,[3] indoles using cobalt carbonyl,[4] and bicyclic β-lactams with tetrakis(triphenylphosphine)palladium(0) and carbon monoxide.[5] Recently, β-lactams were synthesized by the rhodium(I)-catalyzed carbonylation of aziridines.[6]

The reaction of azirines with nucleophilic reagents has been investigated in some detail.[7,8] A question that arises is whether

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