The coordination chemistry of these ditelluroether ligands will be reported elsewhere in due course.

Reaction of a Terminal Phosphinidene Complex with a Carbene Complex. Synthesis of a Phosphorus–Carbon Double Bond through Phosphinidene–Carbene Coupling

N. Hoa Tran Huy and François Mathey*

Laboratoire CNRS-SNPE, BP 28
*94320 Thiais, France*

Summary: The reaction of (phenylethoxycarbene)pentacarbonyltungsten with transient (phenylphosphinidene)-pentacarbonyltungsten gives (2-ethoxy-1,2-diphenylphosphaethylene)pentacarbonyltungsten. This phosphaalkene complex spontaneously dimerizes to form the corresponding 1,2-diphosphetane complex. This dimerization is reversible upon heating, and the phosphaalkene complex can be trapped as [4 + 2] cycloadducts by 2,3-dimethylbutadiene or cyclopentadiene.

We have recently shown that terminal phosphinidene complexes as generated by thermal or catalytic decomposition of the appropriate 7-phosphanorbornadiene complexes readily react with olefins to give the corresponding phosphirane complexes.[1] Since the M(CO)$_5$ groups (M = Cr, Mo, W) are isolobal with methylene,[2] it seemed possible to mimic this type of cycloadditions by using carbene complexes R$_2$C=M(CO)$_5$ in lieu of olefins in order to obtain, at least transiently, carbon–phosphorus–transition-metal three-membered heterocycles. We describe here our first attempt in this direction. The reaction of equimolar amounts of the 7-phosphanorbornadiene complex 1 with the carbene complex 2 in the presence of catalytic quantities of CuCl affords the 1,2-diphosphetane complex 3[3] in ca 56% yield (eq 1). The empirical formula
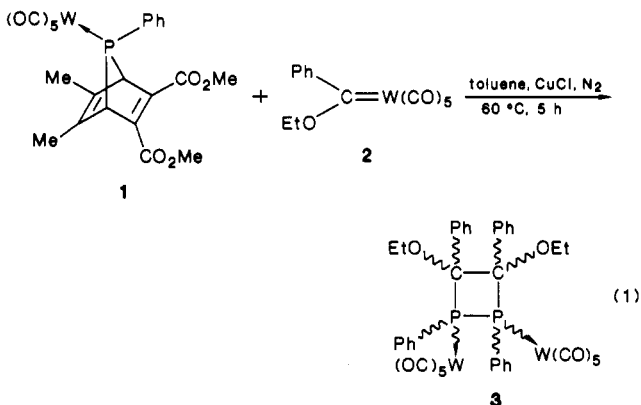
of 3 was easily established by elemental analysis[3] and mass

spectrometry (EI, 70 eV, ^{184}W): m/z (relative intensity) 566 (M/2, 74), 510 (M/2 – 2CO, 47), 481 (M/2 – 3CO – H, 100). That the compound is an unsymmetrical dimer with a P–P bond was shown by its ^{31}P NMR spectrum: AB system, δ −80.06 and −71.10 in CDCl$_3$ (positive for downfield shifts from external 85% H$_3$PO$_4$), ^1J(P–P) = 97.7 Hz. The ^{1}H and ^{13}C NMR spectra[3] confirmed the proposed formulation. The copper chloride serves to lower the decomposition temperature of 1 from ca. 110 to 50–60 °C.[1] This is necessary in view of the limited thermal stability of 2. However, since CuCl does not interfere with the condensation of terminal phosphinidene complexes with olefins, it seems logical to assume that the same holds true in this case. Thus, the most logical mechanism explaining the formation of 3 is that depicted in eq 2.
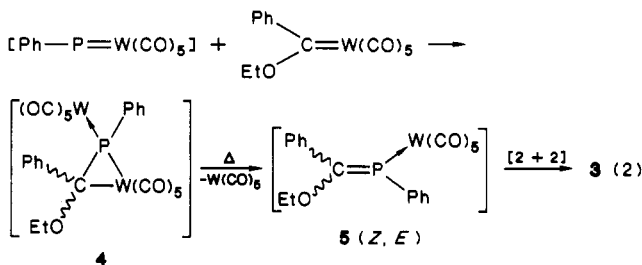
The initial condensation would yield a three-membered ring such as 4 which is analogous to some already known σ,π-complexes of phosphaalkenes.[4] Then, 4 would spontaneously lose the π-bonded W(CO)$_5$ group[5] to give a mixture of the corresponding Z and E phosphaalkene σ-complexes 5. The [2 + 2] dimerization of 5 would ultimately lead to 3.[6]

Another phosphinidene–carbene coupling has been recently described,[7] but in the final product the formal P=C double bond thus formed is incorporated in a cluster and has completely lost its π-bond reactivity. This is not the case here. As suggested by the mass spectral data, the [2 + 2] dimerization leading to 3 is easily reversible upon heating and 3 can be used as a generator of P=C double bonded species. Indeed, the reactions of 3 with 2,3-dimethylbutadiene and cyclopentadiene in sealed tubes at ca. 130 °C in toluene afford the [4 + 2] cycloadducts 6[8]

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(3) Compound 3 was purified by chromatography on Florisil (eluent pentane/CH$_2$Cl$_2$, 5/1). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 14.34 (s, Me), 60.98 (s, OCH$_2$), 65.61 (d, ^1J(C–P) = 11 Hz, O–C–P), 195.38 (cis CO). IR (pentane): ν(CO) 2075 (m), 1955 (vs) cm^{-1}. Anal. Calcd for C$_{40}$H$_{30}$O$_{12}$P$_2$W$_2$: C, 42.44; H, 2.65; P, 5.48; W, 32.49. Found: C, 42.23; H, 2.65; P, 5.2; W, 33.0.

(4) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mitschler, A. *J. Am. Chem. Soc.* 1984, *106*, 826.

(5) Similar losses have been described in the literature; for example, (PhP=PPh) [Cr(CO)$_5$]$_3$ loses its π-bonded Cr(CO)$_5$ upon heating to give [Ph-Ṗ→Cr(CO)$_5$]$_2$: Borm, J.; Zsolnai, L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* 1983, *22*, 977.

(6) Similar Z + E "head to head" dimerizations have been described for RP=C(Ph)OSiMe$_3$: Becker, G.; Becker, W.; Uhl, G.; Uhl, W.; Wessely, H.-J. *Phosphorus Sulfur* 1983, *18*, 7. See also: Becker, G.; Becker, W.; Mundt, O. *Phosphorus Sulfur* 1983, *14*, 267.

(7) Williams, G. D.; Geoffroy, G. L.; Whittle, R. R. *J. Am. Chem. Soc.* 1985, *107*, 729.

(8) Compounds 6a,b were purified by chromatography on silica gel at −10 °C (eluent pentane/CH$_2$Cl$_2$, 8/1). ^{31}P NMR (CDCl$_3$): δ +5.4 and +7.4. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 15.32 (s, OCH$_2$CH$_3$), 20.17 (s, Me), 21.53 (d, ^3J(C–P) = 8.5 Hz, Me), 33.32 (d, ^1J(C–P) = 24.4 Hz, CH$_2$P), 40.80 (d, ^2J(C–P) = 3.7 Hz, CH$_2$), 58.22 and 58.76 (2s, OCH$_2$), 79.85 (d, ^1J(C–P) = 39 Hz, C–P), 123.01 (d, J(C–P) = 3.7 Hz, =CMe), 197.14 (d, ^2J(C–P) = 7.3 Hz, cis CO). MS (EI, 70 eV, ^{184}W): m/z (relative intensity) 648 (M, 87), 508 (M – 5CO, 100). IR (CH$_2$Cl$_2$): ν(CO) 2075 (m), 1942 (vs) cm^{-1}. Anal. Calcd for C$_{26}$H$_{25}$O$_6$PW: C, 48.16; H, 3.86; O, 14.82; P, 4.78; W, 28.38. Found: C, 47.92; H, 3.99; O, 15.11; P, 4.53; W, 28.30. One isomer (δ(^{31}P) +5.4) has been obtained in the pure state by slow recrystallization from CH$_2$Cl$_2$/pentane (4/1): mp 177–179 °C; ^{1}H NMR (CDCl$_3$): δ 1.25 (t, ^3J(H–H) = 6.8 Hz, 3 H, OCH$_2$CH$_3$), 1.78 (s br, 3 H, Me), 1.94 (s br, 3 H, Me), 2.72 (m, 2 H, CH$_2$P), 2.84 (m, 2 H, CH$_2$), 3.30 (q, 2 H, OCH$_2$).

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(1) Marinetti, A.; Mathey, F. *Organometallics* 1984, *3*, 456. Marinetti, A.; Charrier, C.; Mathey, F.; Fischer, J. *Organometallics* 1985, *4*, 2134.
(2) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* 1982, *21*, 711. Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 89.

and 7,[9] both as mixtures of two isomers (eq 3 and 4). These [4 + 2] cycloadditions are typical of either free or P-complexed P=C double bonds.[10,11]
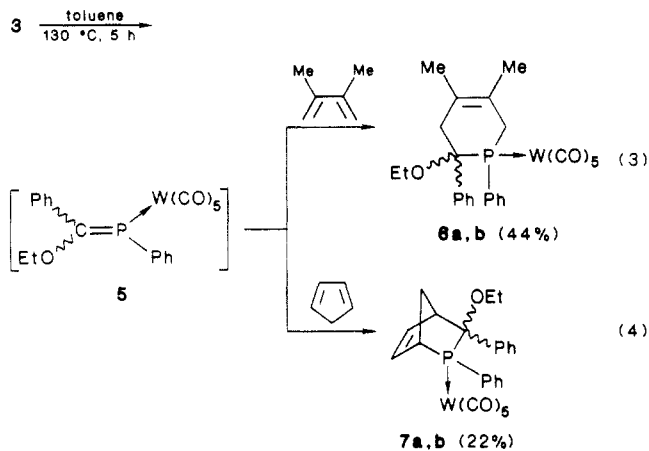
We are currently exploring the various possibilities offered by these preliminary results.

(9) Complexes 7a,b were separated by chromatography on silica gel at –10 °C (eluent pentane/CH_2Cl_2, 7/1). 7a: mp ~115 °C; ^{31}P NMR ($CDCl_3$) δ +55.4; ^{1}H{^{31}P} NMR ($CDCl_3$) δ 1.32 (t, 3 H, CH_3), 2.14 (m, ^2J(H–H) = 10.3 Hz, 1 H, bridge CH_2), 2.66 (m, 1 H, bridge CH_2), 3.38 (m, 1 H, OCH_2), 3.60 (m, 1 H, OCH_2), 3.70 (m, 2 H, bridgehead CH), 6.16 (m, ^3J(H–H) = 5.6 Hz, 1 H, =CH), 6.31 (m, ^3J(H–H) = 5.6 Hz, 1 H, =CH), 6.45–7.54 (m, 10 H, Ph); IR (CH_2Cl_2) ν(CO) 2072 (m), 1940 (vs) cm^{-1}; MS (EI, 20 eV, ^{184}W) m/z (relative intensity) 632 (M, 47), 548 (M – 3CO, 100), 492 (M – 5CO, 89). Anal. Calcd for $C_{25}H_{21}O_6PW$: C, 47.48; H, 3.32; O, 15.19; P, 4.90; W, 29.09. Found: C, 47.79; H, 3.35; O, 15.34; P, 4.43; W, 28.90. 7b (major isomer) mp 147–150 °C; ^{31}P NMR ($CDCl_3$) δ +44.6 (^1J(^{31}P–^{183}W) = 239 Hz); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 14.70 (s, Me), 42.83 (d, ^2J(C–P) = 15 Hz, bridge CH_2), 48.61 (d, ^1J(C–P) = 14 Hz, CH–P), 49.65 (d, ^2J(C–P) = 4 Hz, CH), 61.12 (d, ^3J(C–P) = 4 Hz, OCH_2), 90.27 (d, ^1J(C–P) = 34 Hz, O–C–P), 196.61 (d, ^2J(C–P) = 5 Hz, cis CO), 199.52 (d, ^2J(C–P) = 23 Hz, trans CO); ^{1}H{^{31}P} NMR δ 0.90 (t, 3 H, CH_3), 2.31 (m, 2 H, bridge CH_2), 3.08 (q, 2 H, OCH_2), 3.86 (m, 2H, bridgehead CH), 6.05 (dd, ^3J(H–H) = 5.6 and 3.2 Hz, 1 H, =CH), 6.45 (dd, ^3J(H–H) = 5.6 and 2.9 Hz, 1 H, =CH), 7.24–7.60 (m, 10 H, Ph); IR (CH_2Cl_2) ν(CO) 2072 (m), 1940 (vs) cm^{-1}; MS (EI, 20 eV, ^{184}W) m/z (relative intensity) 632 (M, 39), 548 (M – 3CO, 100), 492 (M – 5CO, 65). Anal. Found: C, 47.24; H, 3.45; O, 15.25; P, 4.05; W, 28.90. We suggest that in the minor isomer 7a, the OCH_2 is cis to the W(CO)$_5$ group, thus explaining the deshielding and the inequivalency of these protons (hindered rotation); conversely, one of the bridge protons of 7a is shielded by the phenyl C substituent.

(10) Arbuzov, B. A.; Dianova, E. N. *Phosphorus Sulfur* 1986, 26, 203.

(11) Deschamps, B.; Mathey, F. *J. Chem. Soc., Chem. Commun.* 1985, 1010.

## Asymmetric Recognition between Triosmium Clusters and Their μ-Acyl Ligands

Merritt C. Helvenston and Thomas J. Lynch*

*Department of Chemistry, University of Nevada
Reno, Nevada 89557-0020*

Summary: The triosmium clusters $Os_3(1,2$-μ-H)[1,2-μ-O=C(CHMeR)](CO)$_{10}$ (R = Et (1), Ph (2), or cyclohexyl (3)) exist as diastereomers resulting from the combined cluster-centered asymmetry and the asymmetry of the α-acyl carbon. The diastereomeric excesses (de) of the triosmium clusters, as synthesized, are 18%, 81%, and 15%, respectively. The diastereomers of 3 are separable by thin-layer chromatography. Each diastereomer of 3 independently equilibrates to a de of 20% when heated in the presence of 1,4-diazabicyclo[2.2.2]octane. Clusters 1 and 2 give thermodynamic de's of 8% and 58%, respectively, under the same equilibrating conditions.

When a heterobidentate ligand is bound to a trinuclear cluster, such as in structure A, the compound exists as a pair of enantiomers as a result of the cluster-centered asymmetry. A variety of such di- and trimetal complexes containing heterobidentate ligands have been reported.[1-7] When the ligand is also asymmetric, diastereomers result that may have significantly different stabilities due to interactions between the metal cluster moiety and the bridging ligand; see structure B. These energy differences
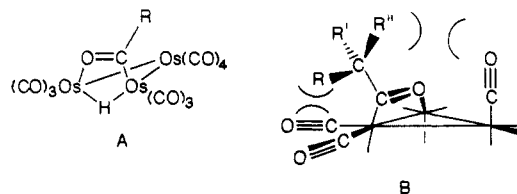
will determine the suitability of clusters for asymmetric synthesis and catalysis and for the use of chiral clusters as mechanistic probes for cluster integrity under catalytic conditions. We now report results which demonstrate the cooperative asymmetric recognition between triosmium clusters and their μ-acyl ligands. Stepwise asymmetric induction has recently been reported on mononuclear titanium,[8] iron,[9-12] rhenium,[13] and cobalt,[14] complexes. Asymmetric syntheses using mononuclear organometallic catalysts have been reviewed.[15]

Cluster 1 was prepared by the method of Mayr[16] by titrating $Os_3(CO)_{12}$ in dry tetrahydrofuran with *sec*-BuLi (1.3 M in cyclohexane) while monitoring by IR ν(CO). The resulting anion was protonated with $F_3CC(O)OH$ to yield 1. Clusters 2 and 3 were synthesized by the reaction of $Os_3(NCMe)_2(CO)_{10}$[4] with an excess of either (±)-2-phenylpropionaldehyde (Oxford) or (±)-2-cyclohexylpropionaldehyde, respectively[17] in dibutyl ether at 80 °C

(1) Yu, Y. F.; Gallucci, J.; Wojcicki, A. *J. Am. Chem. Soc.* 1983, 105, 4826–8.

(2) Staal, L. H.; van Koten, G.; Vrieze, K.; van Santen, B.; Stam, C. H. *Inorg. Chem.* 1981, 20, 3598–606.

(3) Adams, R. D.; Dawoodi, Z. *J. Am. Chem. Soc.* 1981, 103, 6510–2. Benoit, A.; Darchen, A.; Le Marouille, J. Y.; Mahé, C.; Patin, H. *Organometallics* 1983, 2, 555–8.

(4) Aime, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* 1983, 1807–9.

(5) Longato, B.; Martin, B. D.; Norton, J. R.; Anderson, O. P. *Inorg. Chem.* 1985, 24, 1389–94.

(6) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kampe, C. E.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* 1984, 23, 4640–5.

(7) Lin, Y. C.; Mayr, A.; Knobler, C. B.; Kaesz, H. D. *J. Organomet. Chem.* 1984, 272, 207–29.

(8) Reetz, M. T.; Kyung, S. H.; Westermann, J. *Organometallics* 1984, 3, 1716–7.

(9) Baird, G. J.; Davies, S. G.; Maberly, T. R. *Organometallics* 1984, 3, 1764–5.

(10) Baird, G. J.; Bandy, J. A.; Davies, S. G.; Prout, K. *J. Chem. Soc., Chem. Commun.* 1983, 1202–3.

(11) Davies, S. G.; Walker, J. C. *J. Chem. Soc., Chem. Commun.* 1985, 209–10.

(12) Liebeskind, L. S.; Welker, M. E. *Organometallics* 1983, 2, 194–5.

(13) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1985, 107, 4103–4.

(14) Theopold, K. H.; Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* 1982, 104, 5250–2.

(15) Kagan, H. B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8, Chapter 53.

(16) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.* 1982, 21, 1704–6.

(17) The $Os_3(NCMe)_2(CO)_{10}$ was purified by silica gel column chromatography (CH_2Cl_2 eluant), and the aldehydes were distilled immediately before use. A solution of $Os_3(NCMe)_2(CO)_{10}$ in dibutyl ether (10 mg/mL) was treated with 3–5 equiv of aldehyde. Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* 1981, 216, C56–C60.