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Oxidation of 1,2-Diphenyl-3,4-diphosphinidenecyclobutene on the Group-6 Metal Tetracarbonyl Complexes[#]

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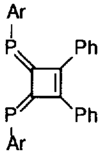
Abstract: The group-6 metal(0) tetracarbonyl complexes of a sterically protected 3,4-diphosphinidenecyclobutene were irradiated with light in the presence of oxygen to give tetracarbonyl[2,3-dibenzoyl-1,4-diphospha-1,3-butadiene]metal(0) complexes, and the structures were confirmed by X-ray analysis. © 1997 Elsevier Science Ltd. All rights reserved.

Using an extremely bulky 2,4,6-tri-*t*-butylphenyl group (hereafter, abbreviated to the Ar group), we were successful in the preparation of several kinds of unusual organophosphorus compounds[1] such as diphosphenes,[2a,b] phosphaalkenes,[2c] and phosphacumulenes[2d,e] as stable species. Appel,[3] Märkl,[4] and we,[5] independently, prepared some sterically protected diphosphinidenecyclobutenes **1**—**3** as an additional example of low coordinated organophosphorus compounds. These compounds are a phosphorus analogue of dimethylenecyclobutene and can be considered as 1,4-diphospha-1,3-butadiene and/or 1,6-diphosphahexa-1,3,5-triene bearing two low-coordinated phosphorus atoms. We have shown that there is an equilibrium between **2** and **3** due to the rotation around the P–C double bond upon irradiation with light. Halogen-induced isomerization has also been found to proceed in the presence of a catalytic amount of iodine.[5c]



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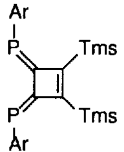

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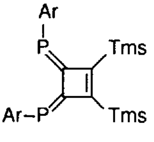

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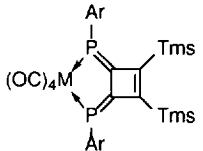
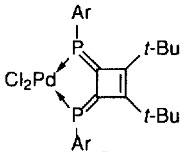


4A—C



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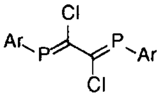

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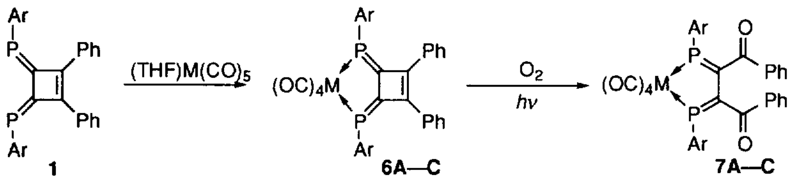
Ar = 2,4,6-*t*-$Bu_3C_6H_2$; Tms = Me_3Si; **A**: M = Cr; **B**: M = Mo; **C**: M = W

Furthermore, we reported on the preparation and structures of the group-6 metal(0) carbonyl complexes such as molybdenum(0) complex **4B**[6] and palladium(II) complex **5**[7] having diphosphinidenecyclobutenes as a bidentate ligand. We have now found that the ligand on the group-6 metal(0) tetracarbonyl complexes **6** undergoes an oxidation reaction with molecular oxygen upon exposure to light to give [2,3-dibenzoyl-1,4-bis-(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,3-butadiene]metal(0) complexes (**7**) as shown in Scheme 1.



Scheme 1. Ar = 2,4,6-*t*-$Bu_3C_6H_2$; **A**: M = Cr; **B**: M = Mo; **C**: M = W

The 3,4-diphosphinidene-1,2-diphenylcyclobutene **1** was prepared according to the method reported previously and was allowed to react with the group-6 metal(0) carbonyl complexes in THF to give the corresponding complexes **6A**—**C**.[8] A solution of **6A** (39.9 mg, 0.0435 mmol) in benzene (75 mL) was irradiated with a 500-W Xe-lamp through a Y-49 filter for 4.5 h under an atmosphere of oxygen to give **7A** (33.0 mg, 0.0347 mmol, 80% yield) together with the starting chromium(0) complex **6A** (2.8 mg, 3.05 μmol, 7% recovery). Very similarly, **6B** and **6C** were illuminated in the presence of oxygen for 12 h and 20 h to afford the corresponding tetracarbonyl[2,3-dibenzoyl-1,4-diphospha-1,3-butadiene]metal(0) complexes **7B** and **7C** in 78 and 57% yield, together with recovery of **6B** and **6C** in 6 and 15%, respectively. The complexes **7A–C** were analyzed by spectroscopic data as well as elemental analysis.[9]

Furthermore, the tungsten complex **7C** was analyzed by X-ray crystallography.[10] Figure 1 shows an ORTEP drawing of the molecular structure of **7C** which clearly indicates that 2,3-dibenzoyl-1,4-diphospha-1,3-butadiene ligates on the tungsten atom. The molecule belongs to the space group Aba2, having a C_2 symmetry around the rotation axis passing through W(1) and the midpoint of C(1)–C(1*). The atoms, W(1), P(1), C(1), C(1*), and P(1*), are on the same plane with a mean deviation of 0.015 Å and the dihedral angle C(20)–C(1)–C(1*)–C(20*) is 9°. The two Ar rings [C(2)–C(7) and C(2*)–C(7*)] are almost perpendicular to the WPCCP plane forming an interplanar angle of 90.6°. The carbonyl group, consisting of C(1), C(20), C(21), and O(1), makes a perfect plane forming dihedral angles of 54.5° and 136.9° with the WPCCP and the benzene ring C(2)–C(7), respectively. The phenyl ring of the benzoyl group forms a dihedral angle of 117.5° with the WPCCP

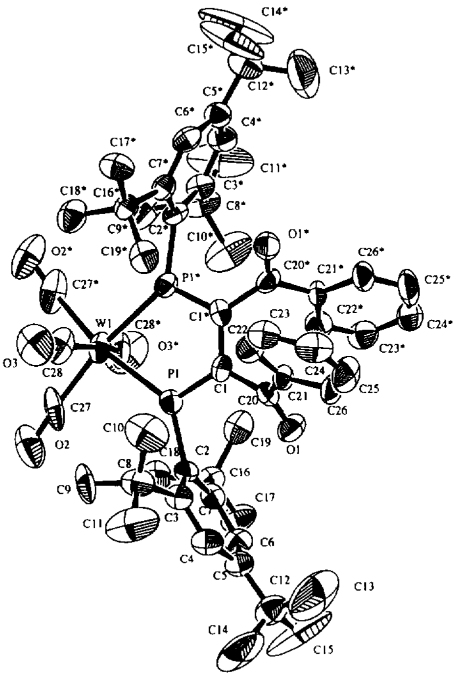


Figure 1. Molecular structure of tungsten complex **7C**. Some selected bond lengths (Å) and bond angles (°): W(1)–P(1), 2.454(4); W(1)–C(27), 2.00(1); W(1)–C(28), 2.10(1); P(1)–C(1), 1.693(9); P(1)–C(2), 1.839(10); O(1)–C(20), 1.21(1); C(1)–C(1*), 1.45(1); C(1)–C(20), 1.53(1); C(2)–C(3), 1.43(1); C(20)–C(21), 1.50(1); P(1)–W(1)–P(1*), 76.2(1); P(1)–W(1)–C(27), 92.3(4); P(1)–W(1)–C(27*), 167.9(5); P(1)–W(1)–C(28), 96.4(3); P(1)–W(1)–C(28*), 94.9(3); C(27)–W(1)–C(27*), 99.4(9); C(27)–W(1)–C(28), 82.8(5); C(27)–W(1)–C(28*), 88.0(5); C(28)–W(1)–C(28*), 165.7(6); W(1)–P(1)–C(1), 114.1(3); W(1)–P(1)–C(2), 138.9(4); C(1)–P(1)–C(2), 107.0(5); P(1)–C(1)–C(1*), 117.8(3); P(1)–C(1)–C(20), 122.6(6); O(1)–C(20)–C(1), 121.2(10); O(1)–C(20)–C(21), 120(1); C(1)–C(20)–C(21), 118.4(9).

plane. The P(1)–W(1) bond length is 2.454(4) Å. The six ligands around the W atom are located as a slightly deformed octahedron. The P=C bond length [1.693(9) Å for P(1)–C(1)] is close to the corresponding values reported for the molybdenum complex **4B** (1.680(4) and 1.686(4) Å).[6b] The bond length for C(1)–C(1*) is 1.45(1) Å and the value is shorter than that for either **2** (1.498(8) Å) or **4B** (1.483(6) Å),[6b] but is similar to that for 2,3-dichloro-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-1,3-butadiene (**8**, 1.445(7) Å).[11] A very similar structure was obtained for **7A** by X-ray crystallographic analysis.[12]

This type of oxidation appears to occur from an excited state of the metal(0) complexes **6** upon irradiation with light to react with ground-state oxygen since the free ligand **1** itself did not react with oxygen.[13] Thus, a control reaction of (*E*,*E*)-**1** (40 mg) in benzene (100 mL) under similar conditions, even in the presence of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (10 mg) as a triplet sensitizer,[14] resulted in the recovery of the starting **1** together with a small amount of isomerized (*E*,*Z*)-**1** due to the *E*/*Z* photo-isomerization.[5a] The complexes **7** are considered as a 2,3-substituted 1,4-diphospha-1,3-butadiene and expected to be converted into further extended derivatives of interest.

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References and Notes

\# Dedicated to Prof. Dr. Dieter Seebach at Eidgenössische Technische Hochschule, Zürich, on the occasion of his 60th birthday.

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8. **6A**: ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ_P = 188.9; IR (KBr)ν / cm^{-1} 2015, 1923, 1900. **6B**: δ_P = 172.8; ν / cm^{-1} 2025, 1923, 1890. **6C**: δ_P = 152.5 (J_{PW} = 257 Hz); ν / cm^{-1} 2019, 1916, 1886.

9. **7A**: Dark green prisms; mp 181 °C (decomp.); ^{31}P{^{1}H} NMR (81 MHz, CDCl$_3$) δ_P =276.0 ; ^{1}H NMR (600 MHz, CDCl$_3$) δ = 1.30 (s, 18H, *p-t*-Bu), 1.57 (s, 36H, *o-t*-Bu), 7.03 (dd, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HH}$ = 8.3 Hz, 4H, *m*-Ph), 7.07 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.6 Hz, 4H, *o*-Ph), 7.24 (brs, 4H, ArH), 7.27 (tt, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HH}$ = 1.6 Hz, 2H, *p*-Ph); ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ = 31.1 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.3 (s, *o*-C$\underline{\mathrm{Me}}_3$), 35.1 (s, *p*-$\underline{\mathrm{C}}Me_3$), 39.1 (s, *o*-$\underline{\mathrm{C}}Me_3$), 121.9 (s, *m*-Ar), 127.1 (s, *m*-Ph), 128.0 (brs, *ipso*-Ar), 130.3 (s, *o*-Ph), 132.6 (s, *p*-Ph), 135.7 (s, *ipso*-Ph), 152.2 (s, *p*-Ar), 157.8 (s, *o*-Ar), 175.4 (pseudo t, J_{PC} = 20.9 Hz, P=C), 191.5 (brs, C=O), 213.3 (brs, CO), 228.1 (brs, CO); UV (CH$_2$Cl$_2$) λ_{max} / nm (log ε) 254 (4.80), 440 (4.02), 491 (3.98); IR (KBr) ν / cm^{-1} 2021, 1950, 1925, 1660; MS (FAB) *m/z* 950 (M$^+$); Found: C, 70.47; H, 7.15%. Calcd for $C_{56}H_{68}CrO_6P_2$: C, 70.72; H, 7.21%. **7B**: Moss green prisms; mp 191 °C (decomp.); δ_P = 251.9; ^{1}H NMR (CDCl$_3$) δ = 1.29 (s, 18H, *p-t*-Bu), 1.56 (brs, 36H, *o-t*-Bu), 7.05 (dd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{HH}$ = 8.3 Hz, 4H, *m*-Ph), 7.09 (dd, $^{3}J_{HH}$ = 8.3 Hz, $^{4}J_{HH}$ = 1.3 Hz, 4H, *o*-Ph), 7.20 (brs, 4H, ArH), 7.27 (tt, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, *p*-Ph); ^{13}C{^{1}H} NMR (CDCl$_3$) δ = 31.1 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.4 (s, *o*-C$\underline{\mathrm{Me}}_3$), 35.0 (s, *p*-$\underline{\mathrm{C}}Me_3$), 39.2 (s, *o*-$\underline{\mathrm{C}}Me_3$), 121.7 (s, *m*-Ar), 127.1 (s, *m*-Ph), 127.4 (brs, *ipso*-Ar), 130.4 (s, *o*-Ph), 132.6 (s, *p*-Ph), 135.7 (s, *ipso*-Ph), 152.0 (s, *p*-Ar), 157.6 (s, *o*-Ar), 174.4 (pseudo t, J_{PC} = 20.9 Hz, P=C), 192.7 (brs, C=O), 201.6 (brs, CO), 216.6 (brs, CO); UV (CH$_2$Cl$_2$) λ_{max} / nm (log ε) 253 (4.87), 430 (4.07), 485 (4.12); IR ν / cm^{-1} 2035, 1955, 1928, 1662; MS (FAB) *m/z* 996 (M$^+$); Found: C, 67.62; H, 7.01%. Calcd for $C_{56}H_{68}MoO_6P_2$: C, 67.60; H, 6.89%. **7C**: Dark green prisms; mp 219 °C (decomp.); δ_P = 222.5 (J_{PW} = 281 Hz); ^{1}H NMR (CDCl$_3$) δ = 1.29 (s, 18H, *p-t*-Bu), 1.57 (s, 36H, *o-t*-Bu), 7.04 (dd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{HH}$ = 8.2 Hz, 4H, *m*-Ph), 7.08 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.3 Hz, 4H, *o*-Ph), 7.23 (brs, 4H, ArH), 7.27 (tt, $^{3}J_{HH}$ = 7.2 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H, *p*-Ph); ^{13}C{^{1}H} NMR (CDCl$_3$) δ = 31.1 (s, *p*-C$\underline{\mathrm{Me}}_3$), 34.4 (s, *o*-C$\underline{\mathrm{Me}}_3$), 35.1 (s, *p*-$\underline{\mathrm{C}}Me_3$), 39.2 (s, *o*-$\underline{\mathrm{C}}Me_3$), 121.9 (s, *m*-Ar), 126.6 (pseudo t, J_{PC} = 5.6 Hz, *ipso*-Ar), 127.1 (brs, *m*-Ph), 130.3 (s, *o*-Ph), 132.6 (s, *p*-Ph), 135.9 (s, *ipso*-Ph), 152.0 (s, *p*-Ar), 157.7 (s, *o*-Ar), 174.0 (pseudo t, J_{PC} = 23.4 Hz, P=C), 192.1 (pseudo t, J_{PC} = 5.7 Hz, C=O); UV (CH$_2$Cl$_2$) λ_{max} / nm (log ε) 253 (4.87), 432 (4.10), 472 (4.12); IR ν / cm^{-1} 2033, 1948, 1923, 1662; MS (FAB) *m/z* 1082 (M$^+$); Found: C, 62.28; H, 6.32%. Calcd for $C_{56}H_{68}O_6P_2W$: C, 62.11; H, 6.33%.
10. *Crystal Data for 7C*: Recrystallized from benzene-hexane, $C_{56}H_{68}O_6P_2W$, *M*r = 1082.95, orthorhombic, *a* = 18.990(3) Å, *b* = 23.289(4) Å, *c* = 12.042(3) Å, *V* = 5325(2) Å^3, Aba2 (#41), *Z* = 4, *T* = 296 K, *R* = 0.032, *Rw* = 0.028; 1930 unique reflections with $I > 3\sigma(I)$. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically; the rest were included in fixed positions. The structure was solved with teXsan; *Crystal Structure Analysis Package*, Molecular Structure Corporation (1985 & 1992). Further details of the crystal structure investigation for **7C** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).
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12. Crystal data for **7A** will be published elsewhere.
13. Complexes **4A–C**, in contrast to **6A–C**, were stable toward oxygen under similar conditions.
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