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Synthesis and Structure of an (η^4-1-Phosphatrimethylenemethane)ruthenium Complex

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Summary: The ring-opening of (1-phenyl-2-isopropylidenephosphirane)pentacarbonyltungsten upon heating with [$Ru_3(CO)_{12}$] affords a mixture of two isomers of [η^4-3,3-dimethyl-1-phenyl-1-pentacarbonyltungsten-1-phosphatrimethylenemethane]tricarbonylruthenium. The X-ray analysis of one of these isomers shows that the phosphatrimethylenemethane ligand adopts an umbrella shape, is bound in an η^4 fashion, and is staggered relative to the three carbonyl ligands of ruthenium.

Trimethylenemethanes (TMMs) and their equivalents are versatile reactive intermediates for the synthesis of five-membered rings via highly chemo-, regio-, diastereo-, and enantioselective [3+2] cycloadditions. They represent important building blocks for the synthesis of natural product frameworks.[1-3] TMMs are usually generated from methylenecyclopropanes by thermal or transition-metal-catalyzed ring-opening reactions. By reaction with suitable transition metals, methylenecyclopropanes can afford stable TMM complexes.[4,5] The mechanism of this reaction has been studied: complexation of the double bond and subsequent disrotatorary ring-opening is the generally accepted pathway.[6,7]

Meanwhile, the ring-opening of the heteroatom analogues, such as alkylidenethiiranes[8] and alkylidenesiliranes,[9,10] has been reported by Ando and co-workers that could isolate stable iron and ruthenium complexes of the heterotrimethylenemethanes. Phosphatrimethylenemethanes have never been observed either as reactive intermediates or as stable complexes. In fact, they represent one of the few remaining classes of hydrocarbon π-complexes that have no phosphorus equivalents.[11] We report here the first approach to such complexes via ring-opening of a methylenephosphirane derivative.

2-Alkylidenephosphirane−$W(CO)_5$ complexes are easily prepared by addition of terminal phosphinidene complex [R−P−$W(CO)_5$] to allene derivatives.[12] A mixture of [1-phenyl-2-isopropylidenephosphirane]$W(CO)_5$ (**1**)[12] and [$Ru_3(CO)_{12}$] was heated at 100 °C in toluene for 48 h. The reaction was monitored by ^{31}P NMR; the formation of new compounds was shown by the appear-

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[12] Complex **1** was prepared from [Ph−P−$W(CO)_5$] with an excess of 1,1-dimethylallene, as described in: Krill, S.; Wang, B.; Hung, J.-T.; Horan, C. J.; Gray, G. M.; Lammertsma, K. *J. Am. Chem. Soc.* **1997**, *119*, 8432.

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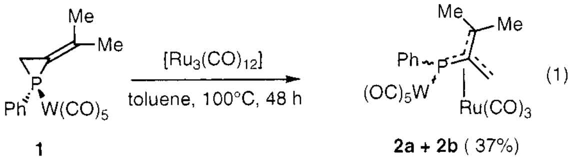
ance of two signals downfield with respect to the starting phosphirane at 28.9 and 34.5 ppm (eq 1).



(1)

1

2a + 2b (37%)
ratio 1:1

After removal of the solvent in vacuo, the residue was purified by chromatography on silica gel with 4:1 hexane/dichloromethane as the eluent to afford a mixture of the two isomeric trimethylenemethane complexes **2a**/**2b** in a 1:1 ratio as pale yellow microcrystals (37% yield). The mixture was characterized by spectrocospic means.[13] The ^{13}C NMR data are particularly informative with three sets of signals at δ 45.2 ($^2J_{CP}$ = 23.9 Hz)/45.7(s) (CH_2), 95.1($^2J_{CP}$ = 12.1 Hz)/96.6 ($^2J_{CP}$ = 5.9 Hz) (CMe_2); 103.6 ($^1J_{CP}$ = 30.4 Hz)/106.1 ($^1J_{CP}$ = 27.5 Hz) (C_2). Similar chemical shifts have been observed by Ando and co-workers for silatrimethylenemethane complexes.[10] Conclusive evidence was obtained from X-ray analysis of one isomer.[14] A suitable sample of **2a** (δ^{31}P 28.9 ppm) was obtained by recrystallization of the mixture from dichloromethane at −78 °C, which yielded pale yellow monocrystalline cubes. The molecule crystallized in space group $P\bar{1}$; an ORTEP drawing is shown in Figure 1 together with selected bond lengths and angles. The phosphatrimethylenemethane ligand is bound in an η^4-fashion and staggered relative to the ruthenium carbonyl ligands. The bond distances C(2)−P(1), C(2)−C(1), and C(2)−C(3) are 1.824(4), 1.449(5), and 1.424(6) Å, respectively, and fall midway between C−P and C−C single and double bonds. The C(2)−P(1) bond is somewhat longer than the value found in another η^4-1-phosphabutadiene complex previously reported (1.783(8) Å).[15] The cross-conjugate interaction with the C−C double bond may be responsible for this slight elongation. Interestingly, the same effect has been described for η^4-silatrimethylenemethane complexes.[9]

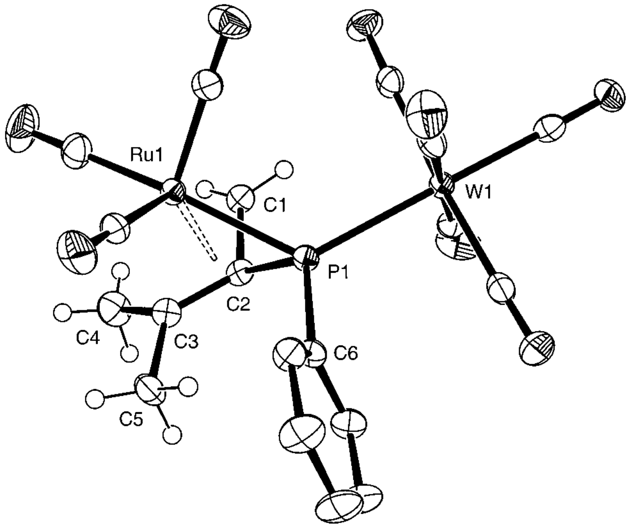


Figure 1. Molecular structure of **2a** in the crystal. Significant bond distances (Å) and angles (deg): W(1)−P(1) 2.525(1), P(1)−Ru(1) 2.431(1), P(1)−C(2) 1.824(4), P(1)−C(6) 1.829(4), C(2)−Ru(1) 2.130(3), C(3)−Ru(1) 2.339(4), C(1)−C(2) 1.449(5), C(2)−C(3) 1.424(6), C(3)−C(4) 1.513(6), C(3)−C(5) 1.509(6); C(2)−P(1)−C(6) 111.4(2), C(2)−P(1)−W(1) 123.8(1), C(2)−P(1)−Ru(1) 58.0(1), Ru(1)−P(1)−W(1) 124.79(4), C(6)−P(1)−W(1) 111.8(1), C(6)−P(1)−Ru(1) 116.7(1), C(1)−C(2)−P(1) 105.5(3), C(3)−C(2)−P(1) 122.4(3), C(3)−C(2)−C(1) 116.9(4), C(4)−C(3)−C(2) 120.1(4), C(5)−C(3)−C(2) 124.6(4), C(5)−C(3)−C(4) 109.5(4).

The central carbon, C(2), lies above the plane of the other three atoms P(1), C(1), and C(3), while planes containing C(6)−P(1)−W(1), H−C(1)−H, and C(4)−C(3)−C(5) are bent away from the Ru(CO)$_3$ fragment. Thus, the η^4-phosphatrimethylenemethane ligand adopts an umbrella shape, as is generally observed in structurally characterized trimethylenemethane[16] and heteroanalogue complexes.[8,17]

In summary, the above results show that methylenephosphiranes can be suitable sources of phosphatrimethylenemethane fragments and open the way to the development of their chemistry.

Supporting Information Available: Crystallographic data for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Phosphirane **1** (0.15 g, 0.3 mmol) and $Ru_3(CO)_{12}$ (0.14 g, 0.22 mmol) in toluene (8 mL) were heated at 100 °C for 48 h. **2a** and **2b** were purified by chromatography on silica gel (hexane−CH_2Cl_2, 4:1), bright yellow microcrystals, yield 76 mg (37%). ^{31}P NMR (C_6D_6): δ 28.9, $^1J_{P-W}$ 232 Hz; 34.5, $^1J_{P-W}$ 235 Hz. ^{13}C NMR (C_6D_6): δ 25.12 (d, $^3J_{C-P}$ = 4.6 Hz, CH_3), 25.86 (d, $^3J_{C-P}$ = 15.1 Hz, CH_3), 26.51(d, $^3J_{C-P}$ = 4.0 Hz, CH_3), 26.84 (s, CH_3); 45.15 (d, $^2J_{C-P}$ = 23.9 Hz, CH_2), 45.68 (s, CH_2); 95.11 (d, $^2J_{C-P}$ = 12.1 Hz, CMe_2), 96.63 (d, $^2J_{C-P}$ = 5.9 Hz, −CMe_2); 103.57 (d,$^1J_{C-P}$ = 30.4 Hz, C−P), 106.06 (d,$^1J_{C-P}$ = 27.5 Hz, C−P), 140.96 (d,$^1J_{C-P}$ = 21.1 Hz, C(Ph)), 141.74 (d,$^1J_{C-P}$ = 13.7 Hz, C(Ph)). MS(^{184}W): m/z 686 (M, 9%), 629 (M − 2CO, 21%), 602 (M − 3CO, 23%), 546 (M − 5CO, 47%), 516 (M − 6CO, 69%), 460 (M − 8CO, 100%). IR (CH_2Cl_2): ν(CO) 2084, 2067, 2057, 2018, 1939 (vs, br) cm^{-1}. Anal. Calcd for $C_{19}H_{13}O_8PRuW$: C, 33.3; H, 1.9. Found: C, 32.5; H, 1.8.

(14) Crystallographic data for $C_{19}H_{13}O_8PRuW$: M = 685.18 g/mol; triclinic; space group $P\bar{1}$; a = 9.4390(8) Å, b = 11.0450(7) Å, c = 11.7080(9) Å, α = 97.915(5)°, β = 97.331(4)°, γ = 113.158(4)°, V = 1089.19(14) Å^3; Z = 2; D = 2.089 g cm^{-3}; μ = 6.085 cm^{-1}; $F(000)$ = 648. Crystal dimensions 0.22 × 0.22 × 0.22. Total reflections collected 7898 and 4545 with $I > 2\sigma(I)$. Goodness of fit on F^2 1.040; $R(I>2\sigma(I))$ = 0.0299, wR2 = 0.0751 (all data); maximum/minimum residual density 1.622(0.174)/−2.046(0.174) e Å^{-3}. Data were collected on a KappaCCD diffractometer at 150.0(1) K with Mo Kα radiation (λ = 0.71073 Å). Full details of the crystallographic analysis are described in the Supporting Information.

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