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THE REACTION OF $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ WITH CARBON DIOXIDE AND DIHYDROGEN: CHARACTERISATION OF $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)\}_2(C_3H_2O_6)]$ USING TWO-DIMENSIONAL NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Summary

$[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ reacts with a mixture of CO_2 and H_2 (1/1, 3 atm) at room temperature to give $[W(PMe_3)_4H_2(\eta^2\text{-}O_2CO)]$ and $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)\}_2(C_3H_2O_6)]$. $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)\}_2(C_3H_2O_6)]$ has been characterised using two-dimensional homo- and hetero-nuclear correlation NMR techniques.

We recently described a study of the preparation [1] and chemistry [2] of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ which led to the syntheses of a range of trimethylphosphine tungsten complexes including carbonyl, dinitrogen, ethylene, diene, formaldehyde, silyl, aquo, hydroxy, fluoro and hydrido derivatives. The reaction of CO_2 with transition metal complexes [3,4] is currently of great interest in view of the improved use of CO_2 as a chemical feedstock. In particular, the interest in discovering potential catalysts which will activate CO_2 and H_2 simultaneously is of importance [3]. We report here on the reaction of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with CO_2 in the presence of H_2.

Results and discussion

$[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ reacts with a mixture of CO_2 and H_2 (1/1, 3 atm) at room temperature to give the previously described compound $[W(PMe_3)_4H_2(\eta^2\text{-}O_2CO)]$ (**1**), [5] and a second compound $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)\}_2(C_3H_2O_6)]$ (**2**), in a molar ratio of 2/3. The formulation of $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)\}_2(C_3H_2O_6)]$ as a dimer is supported by the FAB mass spectrum, which has a group of

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bands corresponding to a W_2 dimer; in particular the band at m/z 1111 corresponds to the parent ion of the $^{184}W_2$-isotopomer less one hydrogen. The infrared spectrum of **2** exhibits strong absorbances at 1614 and 1665 cm^{-1} assignable to carbonyl stretches in functional groups such as formate, carbonate, oxalate, etcetera. There are also bands at 1865 and 1915 cm^{-1} assignable to W–H stretching frequencies.

The $^{31}P\{^1H\}$ NMR spectrum of **2** is complex but the 202.5 MHz two-dimensional ($^{31}P-^{31}P$) COSY-45 NMR spectrum [6] (Fig. 1) immediately indicates the presence of two independent A_2MX spin systems attributable to two isolated WP_4 moieties. The ^1H NMR spectrum is also complex but resonances assignable to two CHO_x, two PCH_2, two WH_2 fragments are observed together with a complex region assigned to PMe resonances (Fig. 2). The $^1H\{^{31}P\}$ NMR spectrum shows the

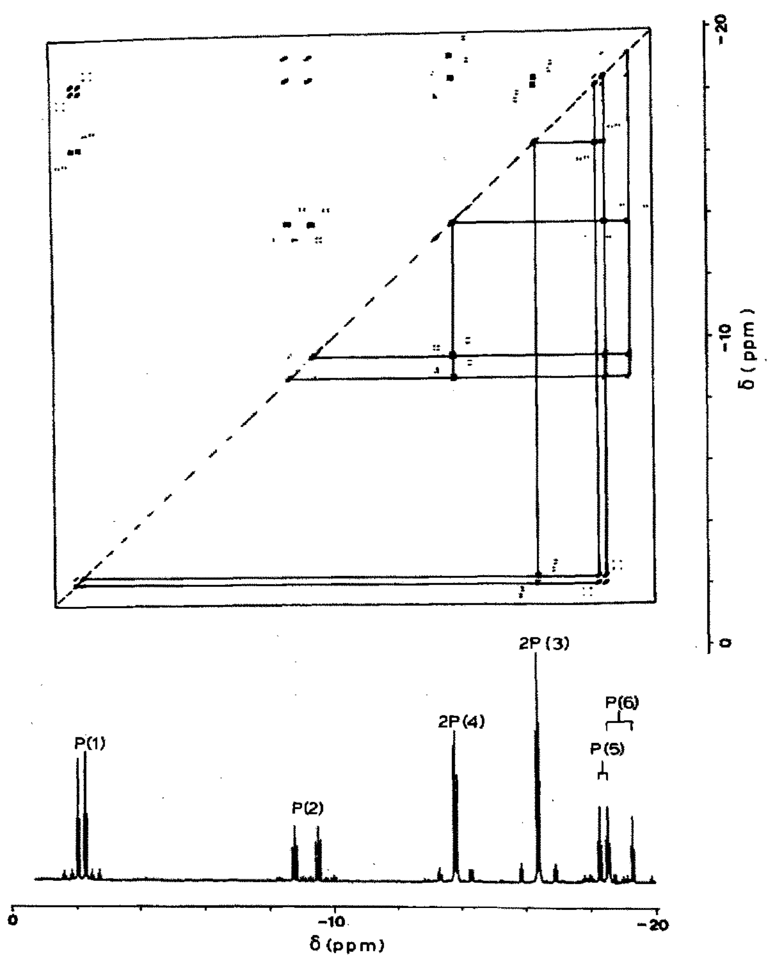


Fig. 1. Two-dimensional $^{31}P-^{31}P$ COSY-45 (202.5 MHz) of **2** (Contour plot) run on a Bruker AM-500 instrument. A (90°-t_1-45°-FID) pulse sequence was used with continuous ^1H decoupling using Waltz-16 modulation. 512t_1 increments each of 2K data points were accumulated using quadrature detection. The spectral width in both dimensions was 3700 Hz. Sine-bell apodisation and zero filling precede Fourier transformation in both dimensions. Symmetrised absolute value spectra are shown.

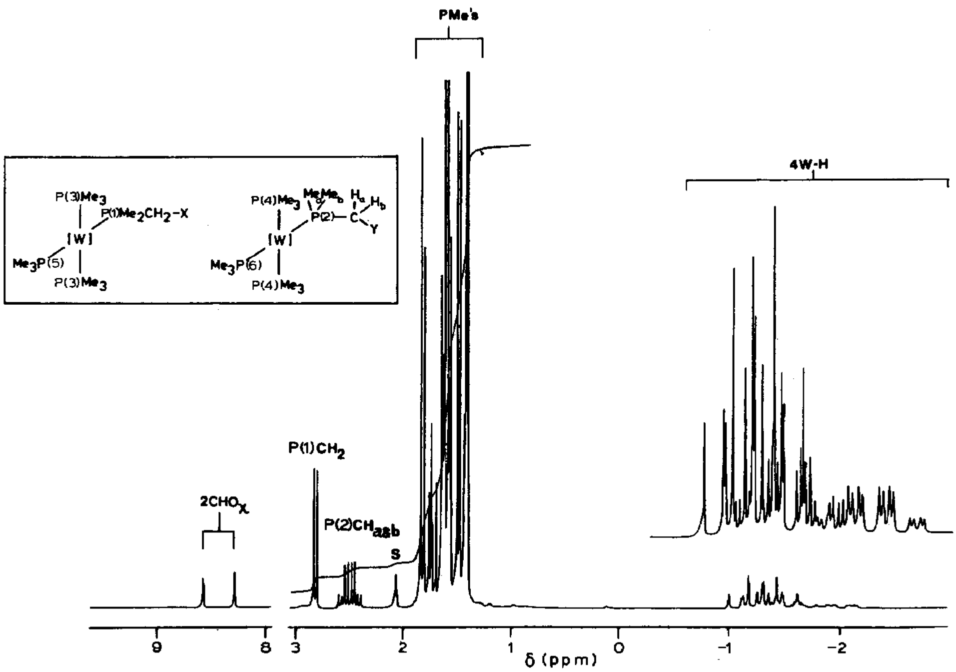


Fig. 2. 300 MHz ^{1}H NMR spectrum of **2** in acetone-d_6 (S denotes solvent).

collapse of much of the multiplet structure and in particular the complex hydride resonances become a singlet and two doublets (J(H–H) 7.5 Hz), assignable to WH_2 and WH_aH_x units. Assignment of the remaining resonances in the ^{1}H NMR spectrum was achieved by a series of selective phosphorus-decoupled ^{1}H NMR experiments. For example, selective irradiation of P(1) indicates that this phosphorus atom is attached to a methylene and two methyl groups.

The ^{13}C NMR spectra (Fig. 3) supported the above formulation with the observation of two doublet of triplets resonances at δ 38.8 and 35.2 ppm, respectively assignable to the PCH_2 groups and doublet resonances at δ 168.4 and 166.8 ppm assignable to the two CHO_x groups. A weak, low field resonance observed at δ 176.5 ppm in the $^{13}C\{^1H\}$ NMR spectrum may be assigned to a carbonyl carbon. It is not possible to determine the multiplicity of all the resonances assigned to the PMe groups in the fully proton-coupled ^{13}C NMR spectrum owing to the complexity of the region. However, vertical slices from the two-dimensional heteronuclear (^{13}C–^1H) J-spectrum (Fig. 4) [6] clearly demonstrate that these resonances are all quartets and that there is no resonance under the solvent. Assignment of the ^{13}C NMR spectrum was achieved by a two-dimensional heteronuclear (^{13}C–^1H) shift correlation NMR experiment (Fig. 5). We were particularly interested to identify a methyl group, $P(2)Me_b$, which was not resolved in the ^{1}H NMR spectrum. This experiment showed that the hydrogens attributable to the $P(2)Me_b$ group were coincident with the resonances attributable to the protons of $P(3)Me_3$.

The NMR experiments described above demonstrate that the molecule possesses the two $\{W(PMe_3)_3(PMe_2CH_2X)H_2\}$ and $\{W(PMe_3)_3(PMe_aMe_bCH_aH_bY)H_aH_x\}$ moieties which are presumed to be linked by an organic fragment which contains

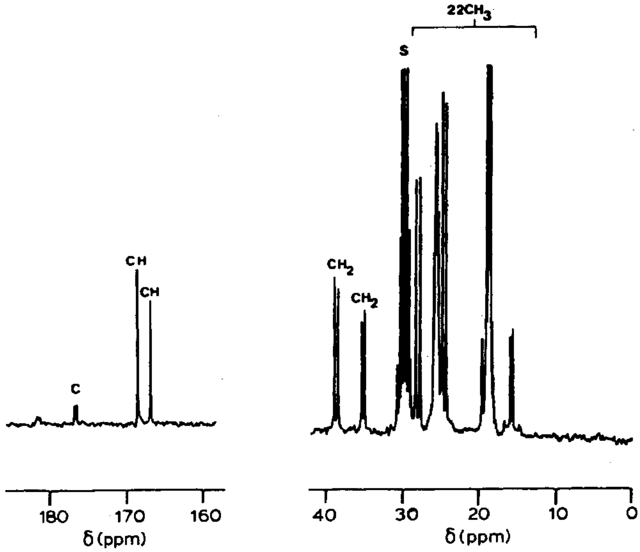


Fig. 3. 62.89 MHz $^{13}C\{^{1}H\}$ NMR spectrum of **2** in acetone-d_6.

CHO_x and HCO_3 groups. ^{183}W satellites are not observed for the resonances assigned to the CHO_x and PCH_2 fragments in the ^1H and ^{13}C NMR spectra and this indicates that these carbon atoms are not bonded to tungsten. We have considered many alternative structures for **2** but evidence is most consistent with the structure shown in Scheme 1. The precise relative disposition of the PR_3, H and

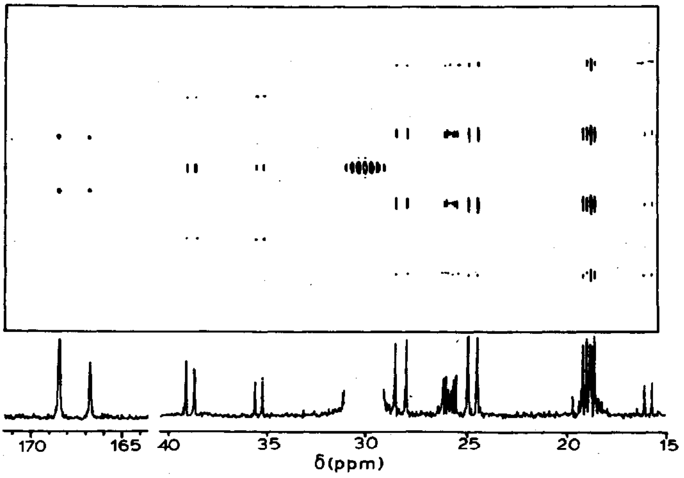


Fig. 4. Two-dimensional ^{13}C–^{1}H heteronuclear J-spectrum of **2** (Contour plot) run on a Bruker AM-250 instrument. A (recycle delay-90°-t_1-180°-t_1-FID) pulse sequence was used. Except for the second t_1 period broad band ^1H decoupling was used throughout. 64t_1 values of 8K data points were accumulated. The spectral width was 260 Hz in f_1 and 11.5 KHz in the f_2 dimension. Sine-bell squared multiplication and zero-filling to 128 points was applied to f_1 and Gaussion weighting to the f_2 dimension prior to Fourier transformation in both dimensions.

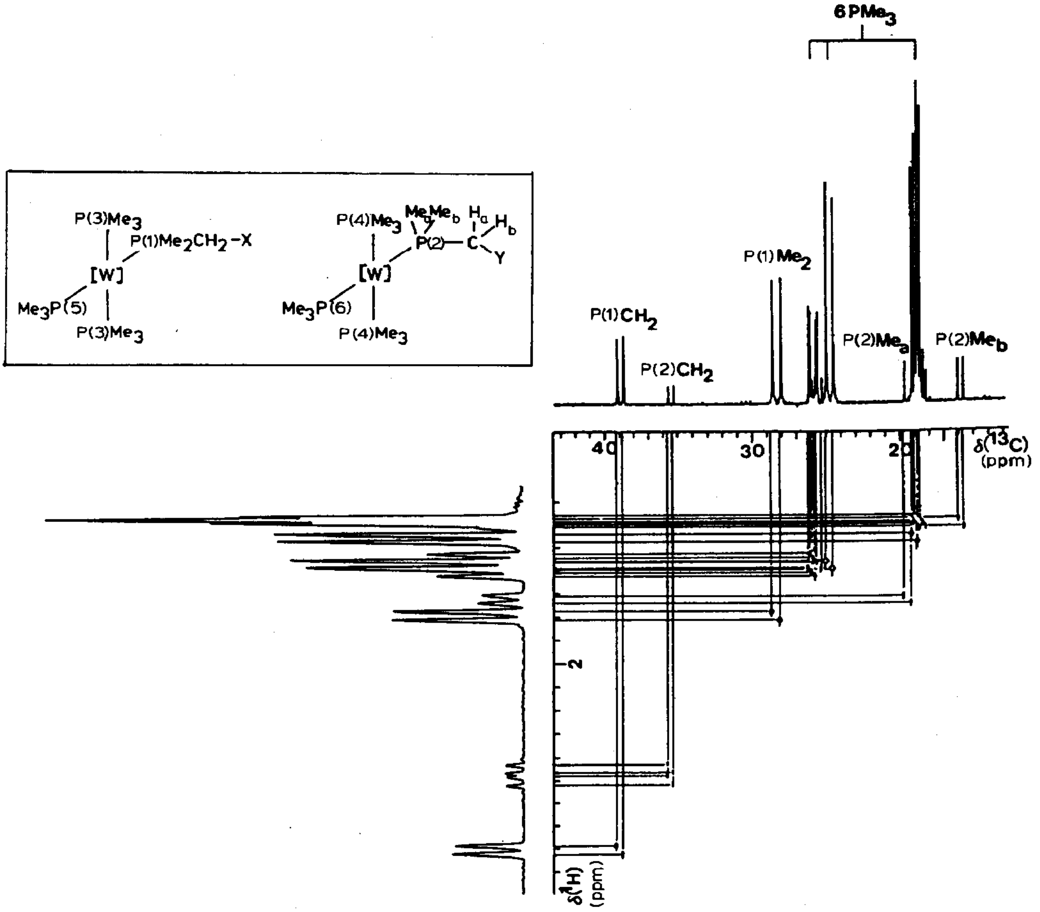
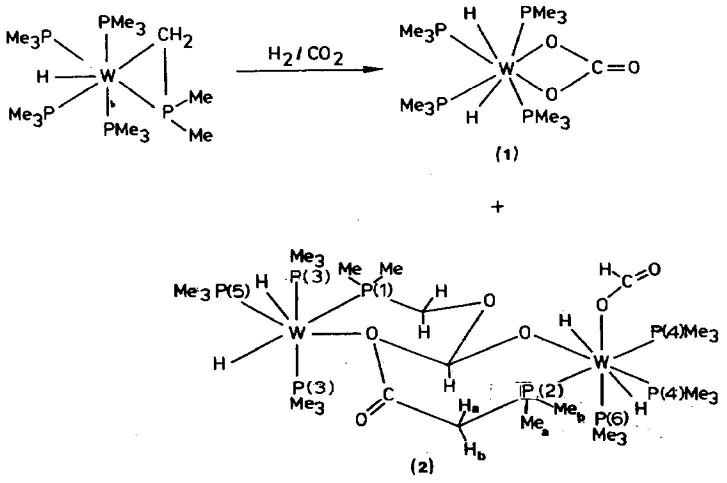


Fig. 5. Two-dimensional ^{13}C–^{1}H heteronuclear shift correlation NMR spectrum of **2** (Contour plot) run on a Bruker AM-250 instrument. 256t_1 increments each of 2K data points were accumulated. The spectral width was 500 Hz in f_1 and 1950 Hz in f_2. Sine-bell squared multiplication and zero-filling to 512 data points was applied to f_1 and Gaussian weighting to the f_2 dimension prior to Fourier transformation in both dimensions.



SCHEME 1

CHO ligands about the tungsten centres are unknown. The formation of carbonato [7], and formato complexes [8] from reactions of CO_2 with transition metal complexes are well documented, as is the coupling of CO_2 to give {[MC(O)OC(O)O} species [9]. The formation of $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)\}_2(C_3H_2O_6)]$ from $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$, CO_2 and H_2 must involve a complex series of reactions, but we envisage that the initial stage corresponds to the insertion of CO_2 into the M–C bond of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ to give a $W^+\text{–}PMe_2CH_2CO_2^-$ moiety. A similar step has been observed for the reaction of $Fe(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H$ with CO_2 [10] and also from the thermolysis of $[Ir(dmpe)_2Cl(CO_2)]$ [11].

Experimental

General

All manipulations of air and/or moisture sensitive materials were carried out in a vacuum or inert atmosphere (N_2 or Ar) line using standard Schlenk techniques or in a dry box under N_2. Reactions involving gases (3 atm) were carried out in glass ampoules sealed with a teflon tap supplied by J. Young (Acton). N_2 and Ar were purified by passage through a gas drying column containing BASF catalyst and 4 Å molecular sieves. All solvents were thoroughly deoxygenated before use by repeated evacuation followed by admission of N_2 (or Ar). Solvents were dried and purified by refluxing over a suitable drying agent, followed by distillation under a N_2 atmosphere. Petroleum ether (b.p. 100–120 °C) was dried over molten sodium; tetrahydrofuran (THF) was dried over molten potassium. Deuterated solvents for NMR samples were stored over activated molecular sieves and transferred by trap-to-trap distillation.

Elemental analyses were carried out in the microanalytical department of the Inorganic Chemistry Laboratory. Nuclear magnetic resonance spectra were recorded on the following instruments: Jeol JNM-PMX60, Bruker AM-250, Bruker WH-300 and Bruker AM-500 instruments. Chemical shifts (δ, ppm; J, Hz) are relative to $SiMe_4$ for ^1H and ^{13}C spectra, and relative to $P(=O)(OMe)_3$ in D_2O for ^{31}P. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), multiplet (m), and virtually coupled multiplet (vcm).

Infrared spectra were recorded on a Perkin–Elmer 1710 FT spectrophotometer. Relative intensities are abbreviated as follows: very strong (vs), strong (s), medium (m), weak (w), broad (br) and shoulder (sh).

Mass spectra were recorded using Fast Atom Bombardment techniques by the mass spectroscopy service of the Dyson Perrins Laboratory here in Oxford.

All two-dimensional NMR experiments were carried out using standard Bruker software and processed using ASPECT 2000 or ASPECT 3000 computers.

The reaction of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with H_2 and CO_2

A solution of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (300 mg, 0.53 mmol) in petroleum ether (b.p. 100–120 °C, 20 cm^3) in a Young's ampoule (150 cm^3) was pressurized with H_2 (1.5 atm) and then CO_2 (3 atm total pressure) and stirred for 3 d at room temperature. A yellow solid was deposited which was separated by filtration, washed with petroleum ether (b.p. 100–120 °C, 20 cm^3) and extracted into THF (20 cm^3). The mixture was filtered, and the orange solution concentrated to ca. 15 cm^3 and placed at −40 and then −80 °C. Pale yellow crystals were deposited and were filtered, washed with THF (2×2 cm^3) at -78°C and dried in vacuo giving $[W(PMe_3)_4(\eta^2\text{-}CO_3)H_2]$ (50 mg, 17%), identified by comparison of ^{1}H NMR and IR spectra with those of an authentic sample [5].

The mother liquor was concentrated to ca. 5 cm^3 and placed at -40 and then -80°C. The pale yellow crystals which formed were separated by filtration, washed with THF (2×2 cm^3) at -78°C and dried in vacuo giving $[\{W(PMe_3)_3(\eta^1\text{-}PMe_2CH_2)H_2\}_2(C_3H_2O_6)]$ (150 mg, 50%).

Elemental analysis, Found (calcd.)(%): C, 28.3 (29.1); H, 6.9 (6.8). Mass spectrum (FAB): m/z 1111, $M^+\{^{184}W\text{-}1H\}$.

NMR data: ^{1}H (at 300 MHz in acetone-d_6, see Fig. 2). 8.57 [1H, d, J(PH) 2, CHO], 8.28 [1H, t, J(PH) 1, CHO], 2.80 [2H, d, J(PH) 9, P(1)CH$_2$], 2.50 [2H, ^{31}P coupled AB quartet, J(PH) 9, P(2) CH$_{ab}$], 1.80 [6H, d, J(PH) 7, P(1)Me$_2$], 1.71 [3H, d, J(PH) 7, P(2)Me$_a$], 1.60–1.45 [54H, complex, $18 \times$ PMe], 1.45 [3H, multiplicity obscured, P(2)Me$_b$], -1.41 [2H, m, (12 lines), J (^{183}W–^{1}H) 49, $2 \times$ W–H], -1.55 [1H, m, (20 lines), $J(H_a\text{–}H_x)$ 7.5, W–H$_{a\text{ or }x}$], -2.05 [1H, m, (20 lines), $J(H_x\text{–}H_a)$ 7.5, W–H$_{x\text{ or }a}$].

^{13}C (at 62.89 MHz in acetone-d_6, see Fig. 3). 176.1 [s, CO], 168.4 [d, CHO], 166.7 [d, CHO], 38.7 [dd, J(PC) 26, PCH$_2$], 35.2 [dd, J(PC) 23, PCH$_2$], 28.0 [d, J(PC) 32 P(1)Me$_2$], 27.0–18.0 [complex, 18 x PMe], 18.5 [d, J(PC) 26, P(2) Me$_a$], 15.7 [d, J(PC) 24, P(2) Me$_b$].

^{31}P{^{1}H} (202.52 MHz, acetone-d_6). -2.16 [1P, dt, J_d(P(1)–P(5)) 47.2, J_t(P(1)–P(3)) 11.0, J(P–W) 214, P(1)], -9.09 [1P, dt, J_d(P(2)–P(6)) 149.4, J_t(P(2)–P(4)) 14.6, J(P–W) 243, P(2)], -13.77 [2P, dd, J_d(P(2)–P(4)) 14.6, J_d(P(4)–P(6)] 10.2, J(P–W) 243, 2P(4)], -16.39 [2P, t, J_d(P(1)–P(3)) = J_d(P(3)–P(5)) 11.0, J(P–W) 264, 2P(3)], -18.41 [1P, dt, J_d(P(1)–P(5)) 47.2, J_t(P(5)–P(3)) 11.0, J(P–W) 243, P(5)), -18.93 [1P, dt, J_d(P(2)–P(6)) 149.4, J_t(P(4)–P(6)) 10.2, J(P–W) 286, P(6)].

Selected infrared data (CsI plates, Nujol mull, cm^{-1}). 1289s, 1301s, 1314s, 1433s, 1614vs, 1665vs, 1856w,br (W–H), 1915 w,br (W–H).

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