

BIS(DIPHENYLPHOSPHINO)ACETYLENE COMPLEXES OF $\text{Cp}(\text{CO})_2\text{Mn}$ AND $(\text{CO})_5\text{M}$ ($\text{M} = \text{Cr}, \text{W}$)

OLLI ORAMA

Department of Chemistry, University of Helsinki, Vuorikatu 20, 00100 Helsinki (Finland)

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Summary

Bis(diphenylphosphino)acetylene (DPPA) reacts with THF complexes of $\text{Cp}(\text{CO})_2\text{Mn}$ and $(\text{CO})_5\text{M}$ ($\text{M} = \text{Cr}, \text{W}$) to yield binuclear diphosphine-bridged complexes of type $[\text{Cp}(\text{CO})_2\text{Mn}]_2\text{DPPA}$ and $[(\text{CO})_5\text{M}]_2\text{DPPA}$. A mononuclear complex $\text{Cp}(\text{CO})_2\text{MnDPPA}$ can be isolated when a 1/1 molar ratio of the reactants is used. The preparation and characterisation of $\text{Cp}(\text{CO})_2\text{MnDPPA}$, $[\text{Cp}(\text{CO})_2\text{Mn}]_2\text{DPPA}$, $[(\text{CO})_5\text{Cr}]_2\text{DPPA}$ and $[(\text{CO})_5\text{W}]_2\text{DPPA}$ are reported, as is the crystal structure of $[\text{Cp}(\text{CO})_2\text{Mn}]_2\text{DPPA}$ determined by X-ray diffraction.

Introduction

Bis(diphenylphosphino)acetylene (DPPA) is a potentially trifunctional ligand, whose coordination capability has been extensively studied [1]. It appears that DPPA normally coordinates via the two phosphorus centres, with the acetylenic bond coordinatively inactive. Thus, even with metal carbonyls such as $(\text{CO})_8\text{Co}_2$, which are especially prone to form acetylene complexes, DPPA gives complexes bond through phosphorus as the isolable products [2]. It is conceivable, however, that DPPA might coordinate via its $\text{C}\equiv\text{C}$ tripple bond if the phosphorus lone pairs were first blocked by strongly coordinated sixteen-electron fragments L_nM . Such compounds, $(\text{L}_n\text{M})_2\text{DPPA}$, might then react via their alkyne function to form heterometallic clusters with $(\text{CO})_8\text{Co}_2$. To test this possibility we prepared $(\text{L}_n\text{M})_2\text{DPPA}$ ($\text{L}_n\text{M} = \text{Cp}(\text{CO})_2\text{Mn}; (\text{CO})_5\text{Cr}; (\text{CO})_5\text{W}$), the synthesis, properties and structure of which are reported.

Results and discussion

The ligand DPPA [3] reacts with the photochemically-produced kinetically labile THF derivatives [4] of $\text{Cp}(\text{CO})_2\text{Mn}$ to yield the complexes 1 or 2 depending on the molar ratio of the starting products.

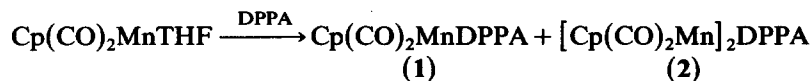
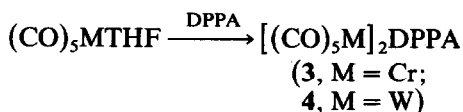


TABLE 1

IR AND NMR SPECTROSCOPIC DATA FOR COMPOUNDS 1-4

Compound	IR $\nu(\text{CO})$ (cm^{-1} ; in CH_2Cl_2)	^{31}P NMR (δ (ppm); J (Hz))	^1H NMR (δ (ppm), J (Hz))
1	1938vs, 1873vs	75.9(s, 1P) - 33.0 (s, 1P)	4.52 (d, 5H, $J(\text{PH})$ 2.2) 7.4-8.0 (m, 20H)
2	1939vs, 1874vs	76.2(s)	4.57 (d, 10H, $J(\text{PH})$ 2.2) 7.4-8.0 (m, 20H)
3	2069sh, 2067m 2016vw, 1988w 1948vs	39.6(s)	7.3-8.0 (m, 20H)
4	2077sh, 2075 2067sh, 1988w 1946vs	- 4.6 $J(\text{PW})$ 301	7.5-8.0 (m, 20H)

From $(\text{CO})_5\text{CrTHF}$ and $(\text{CO})_5\text{WTHF}$, the binuclear compounds **3** and **4**, respectively, are obtained.



Mononuclear species corresponding to **1** could not be obtained in this case; the mononuclear intermediate appears to be an even better ligand than DPPA itself. The compounds **1** to **4** are fully characterized by their analytical (see Experimental section) and spectroscopic data (Table 1).

The IR spectra of **1** and **2** clearly demonstrate the presence of $\text{Cp}(\text{CO})_2\text{Mn}$ groups (Table 1). The $\nu(\text{CO})$ absorptions are independent of whether one (**1**) or two (**2**) $\text{Cp}(\text{CO})_2\text{Mn}$ fragments are coordinated to the ligand. The binuclear compounds **3** and **4** show the $\nu(\text{CO})$ absorption pattern expected for $(\text{CO})_5\text{ML}$ compounds.

The ^1H NMR spectra (Table 1) show the expected phenyl multiplets; and for **1** and **2** the Cp signals are split into doublets, with ($J(\text{PH})$ 2.2 Hz) as would be expected for phosphorus-bound $\text{Cp}(\text{CO})_2\text{Mn}$. The ^{31}P NMR signals of the coordinated phosphorus in **1-4** (Table 1) show high field shifts relative to the signal of the free ligand (δ -32.0) [5]. For **1** the presence of one coordinated (δ 75.9) and one free phosphorus (δ -33.0) is clearly evident. For **4** the phosphorus-tungsten interaction is further indicated by a strong P-W coupling ($J(\text{PW})$ 301 Hz).

The compounds **1** to **4** give clearly resolved mass spectra under EI conditions. The molecular ion is observed in each case. For the manganese derivatives **1** and **2** the base peak corresponds to the molecular ion formed by splittings off of all the CO groups. Further characteristic fragments are formed by loss of PPh_2 or PPh_2C_2 from this ion. The compounds **3** and **4** show the characteristic series of equally spaced $[M^+ - n\text{CO}]$ peaks. An additional series of corresponding peaks caused by primary loss of $(\text{CO})_5\text{W}$, is observed for **4**. For all compounds, peaks for $[\text{Ph}_2\text{PC}_2^+]$ and $[\text{Ph}_2\text{P}^+]$ are observed as characteristic ligand fragments.

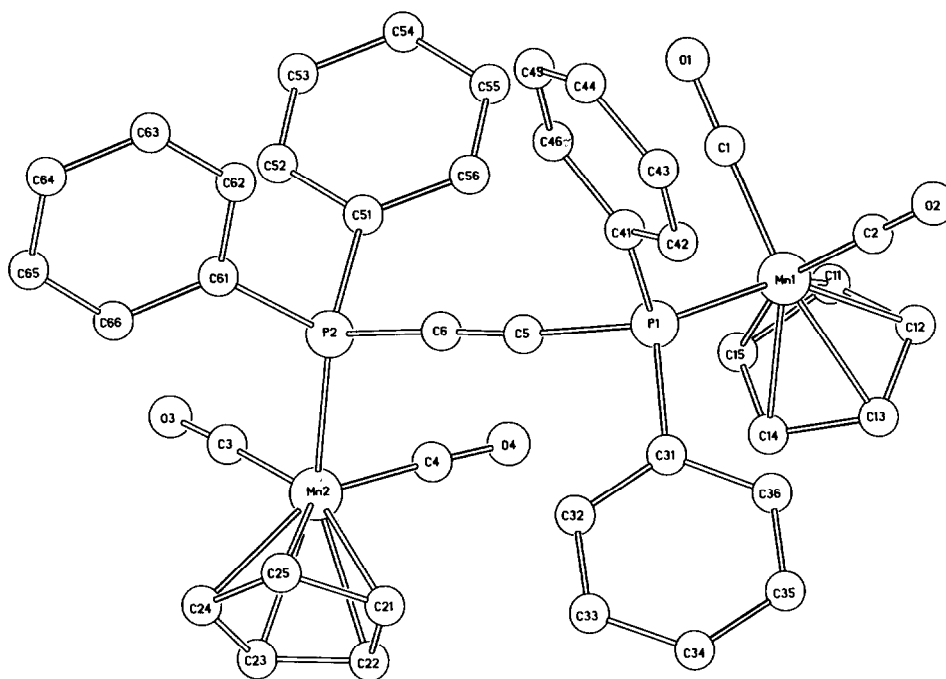
Fig. 1. Molecular structure of **2**.

TABLE 2

SELECTED DISTANCES (pm) AND ANGLES (°) FOR **2**

Mn(1)–P(1)	219.7(2)	P(1)–C(5)	177.3(4)
Mn(2)–P(2)	219.4(2)	P(2)–C(6)	177.4(4)
Mn(1)–C(1)	177.2(4)	C(5)–C(6)	119.9(5)
Mn(1)–C(2)	177.2(4)	Mn–C _{Cp(mean)}	213.1
Mn(2)–C(3)	176.4(4)	C–C _{Cp(mean)}	139.7
Mn(2)–C(4)	175.6(4)	P–C _{Ph(mean)}	182.9
C(1)–O(1)	115.0(5)		
C(2)–O(2)	115.7(5)		
C(3)–O(3)	115.7(5)		
C(4)–O(4)	116.1(5)		
P(1)–Mn(1)–C(1)	90.5(1)	P(2)–Mn(2)–C(3)	93.9(1)
P(1)–Mn(1)–C(2)	92.0(1)	P(2)–Mn(2)–C(4)	89.4(1)
C(1)–Mn(1)–C(2)	92.5(2)	C(3)–Mn(2)–C(4)	91.1(2)
Mn(1)–P(1)–C(31)	118.5(1)	Mn(2)–P(2)–C(51)	117.8(1)
Mn(1)–P(1)–C(41)	118.3(1)	Mn(2)–P(2)–C(61)	122.3(1)
Mn(1)–P(1)–C(5)	111.8(1)	Mn(2)–P(2)–C(6)	111.6(1)
C(31)–P(1)–C(5)	102.6(2)	C(51)–P(2)–C(6)	100.5(2)
C(41)–P(1)–C(5)	101.2(2)	C(61)–P(2)–C(6)	101.4(2)
C(31)–P(1)–C(41)	102.0(2)	C(51)–P(2)–C(61)	99.9(2)
P(1)–C(5)–C(6)	170.3(3)	P(2)–C(6)–C(5)	172.9(3)

Experimental

Structure determination

The cell constants and the reflections were measured on a Syntex-P3 diffractometer with a graphite monochromator, $\lambda(\text{Mo-K}\alpha)$ 71.069 pm. The crystals ($0.3 \times 0.4 \times 0.5$ mm) were monoclinic, space group $P2_1/c$ (No. 14 [6]), $Z = 4$, a 1257.5(4), b 1257.2(4), c 2226.3(8) pm, β 100.83(3)°, V 3456×10^6 pm³, d_{calc} 1.43 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ 9 cm⁻¹, T 233 K, ω -scan, $\Delta\omega = 1.0^\circ$, $1.5 < \omega < 29.3^\circ$ min⁻¹, $1.5 < 2\theta < 45^\circ$, 3608 independent significant reflections ($I < 2\sigma(I)$).

The structure was solved by Patterson synthesis, using the program system SHEL-XTL [7]. The two manganese atoms were successfully located and the non-hydrogen atoms were found in difference Fourier syntheses. After two cycles of refinement the hydrogen atoms were successfully located in difference Fourier maps and the final refinement gave the agreement factors $R_1 = 0.033$ and 0.036 (non-hydrogen atoms with anisotropic temperature factors and the hydrogen atoms with fixed isotropic temperature factors). Figure 1 shows the structure of **2**. Table 2 gives selected distances and angles, and Table 3 the atom coordinates. Lists of thermal parameters and structure factors are available from the author.

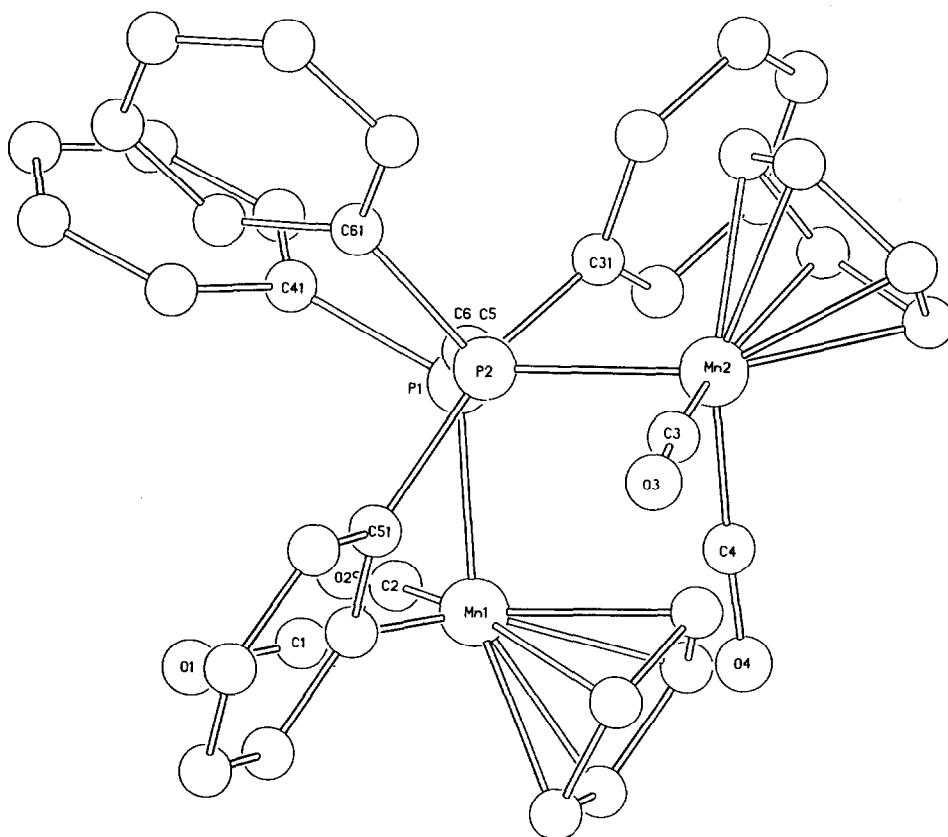


Fig. 2. Molecular structure of **2** along the P-P≡C-P skeleton.

TABLE 3

ATOMIC COORDINATES FOR COMPOUND 2 (with estimated standard deviations in parentheses)

Atom	x	y	z
Mn(1)	0.37339(4)	0.86046(4)	0.41128(2)
Mn(2)	-0.13853(5)	0.81658(5)	0.27392(3)
P(1)	0.31657(7)	0.71472(7)	0.36081(4)
P(2)	-0.06113(7)	0.71837(7)	0.35133(4)
C(5)	0.1741(3)	0.7005(3)	0.3510(2)
C(6)	0.0790(3)	0.7008(3)	0.3517(2)
C(1)	0.3375(3)	0.8075(3)	0.4785(2)
O(1)	0.3143(2)	0.7756(3)	0.5227(1)
C(2)	0.5074(3)	0.8110(3)	0.4306(2)
O(2)	0.5956(2)	0.7810(3)	0.4441(1)
C(3)	-0.2561(3)	0.8393(3)	0.3046(2)
O(3)	-0.3341(2)	0.8587(3)	0.3229(2)
C(4)	-0.0759(3)	0.9296(3)	0.3113(2)
O(4)	-0.0366(3)	1.0065(2)	0.3343(1)
C(11)	0.3274(4)	1.0172(3)	0.4328(2)
C(12)	0.4236(4)	1.0219(4)	0.4113(2)
C(13)	0.4061(4)	0.9833(3)	0.3516(2)
C(14)	0.2967(4)	0.9541(3)	0.3355(2)
C(15)	0.2477(4)	0.9754(3)	0.3858(2)
C(21)	-0.0415(4)	0.7910(5)	0.2068(2)
C(22)	-0.1142(4)	0.8774(4)	0.1883(2)
C(23)	-0.2190(3)	0.8375(4)	0.1817(2)
C(24)	-0.2140(4)	0.7283(4)	0.1948(2)
C(25)	-0.1041(4)	0.6997(4)	0.2103(2)
C(31)	0.3409(3)	0.6994(3)	0.2831(2)
C(32)	0.2714(3)	0.6433(3)	0.2388(2)
C(33)	0.2960(4)	0.6312(4)	0.1811(2)
C(34)	0.3903(4)	0.6753(4)	0.1685(2)
C(35)	0.4597(4)	0.7303(4)	0.2121(2)
C(36)	0.4352(3)	0.7434(3)	0.2698(2)
C(41)	0.3624(3)	0.5863(3)	0.3952(2)
C(42)	0.4542(3)	0.5385(3)	0.3815(2)
C(43)	0.4919(4)	0.4435(4)	0.4086(2)
C(44)	0.4378(4)	0.3957(3)	0.4493(2)
C(45)	0.3483(4)	0.4435(3)	0.4646(2)
C(46)	0.3096(3)	0.5387(3)	0.4378(2)
C(51)	-0.0562(3)	0.7707(3)	0.4285(2)
C(52)	-0.1471(3)	0.7569(3)	0.4550(2)
C(53)	-0.1470(3)	0.7944(3)	0.5129(2)
C(54)	-0.0578(4)	0.8453(3)	0.5455(2)
C(55)	0.0323(3)	0.8609(3)	0.5192(2)
C(56)	0.0332(3)	0.8228(3)	0.4610(2)
C(61)	-0.1039(3)	0.5816(3)	0.3622(2)
C(62)	-0.0433(3)	0.5179(3)	0.4070(2)
C(63)	-0.0788(4)	0.4182(3)	0.4193(2)
C(64)	-0.1755(4)	0.3814(3)	0.3870(2)
C(65)	-0.2349(4)	0.4427(4)	0.3424(2)
C(66)	-0.2005(3)	0.5434(4)	0.3295(2)

The overall structure of **2** is as expected (Fig. 1). The most prominent special feature is a pronounced steric crowding in the neighbourhood of the central $\text{C}\equiv\text{C}$ tripple bond. Apparently it is this crowding which leads to the observed bending of the central $\text{P}-\text{C}\equiv\text{C}-\text{P}$ linkage: the phosphorus atoms are no longer collinear with the acetylenic $\text{C}\equiv\text{C}$ bond, deviating from collinearity by $7.1(3)$ and $9.7(3)^\circ$.

Preparations

All reactions were carried out under dried and purified nitrogen. Solvents were dried by conventional methods, distilled, and stored under nitrogen. Infrared spectra were recorded with a Zeiss Model IMR 40 spectrometer, and mass spectra with a Finnigan MAT 112 or MAT 312 spectrometer at 70 eV. ^1H NMR spectra were measured with a Bruker Model WP 80 FT spectrometer using deuterated acetone as internal standard (acetone- d_6 , 205 ppm), and ^{31}P NMR spectra with a Bruker WP 80 FT spectrometer in toluene at 298 K, rel. 85% H_3PO_4 with $\delta(\text{P}(\text{OMe})_3)$ 139 ppm.

Melting points were determined with a Gallenkamp melting point apparatus for samples in sealed capillaries, and are uncorrected. Pyrex glassware and a Hanau TQ 150 UV lamp were used for photochemical reactions. A Carlo Erba CHN analyser was used for CHN elemental analyses. Silica gel for chromatography was Woelm-Pharma, grain size 0.063–0.200 mm. Freshly sublimed $\text{Cp}(\text{CO})_3\text{Mn}$ was used throughout.

Preparation of **1** and **2**

A solution of 4.7 g (23 mmol) of $\text{Cp}(\text{CO})_3\text{Mn}$ in 300 ml of THF was irradiated for 3.5 h. The yield of $\text{Cp}(\text{CO})_2\text{MnTHF}$ was 70% as determined by IR spectroscopy. To this solution, which contained 16 mmol $\text{Cp}(\text{CO})_2\text{MnTHF}$, was added 6 g (16 mmol) of DPPA for the synthesis of **1** and 3 g (8 mmol) for the synthesis of **2**. The initially red solutions were stirred for 24 h during which they turned yellow. After evaporation of the THF (20°C) the residue was dissolved in toluene and the solution filtered through a layer of silica gel. The filtrate was evaporated to dryness and unchanged $\text{Cp}(\text{CO})_3$ sublimed on to a cold finger at 10^{-2} mbar, 30°C . The product was then chromatographed on silica gel and the separated products were eluted with pentane/toluene.

1. Yield 6.3 g (70%), m.p. 157°C . Found: C, 69.61; H, 4.12. $\text{C}_{33}\text{H}_{25}\text{MnO}_2\text{P}_2$ (570.45) calcd.: C, 69.48; H, 4.41%. MS (m/e (rel. int.)): M^+ 570(4), [$M^+ - 2\text{CO}$] 514(100), [$M^+ - 2\text{CO} - \text{PPh}_2$] 329(48), [$M^+ - 2\text{CO} - \text{PPh}_2\text{C}_2$] 305(19), [PPh_2C_2^+] 209(22), [PPh_2^+] 185(8), [MnCp^+] 120(56), [Mn^+] 55(68).
2. Yield 4.2 g (47%), m.p. 214°C . Found: C, 63.72; H, 3.91. $\text{C}_{40}\text{H}_{30}\text{Mn}_2\text{O}_4\text{P}_2$ (746.51) calcd.: C, 64.34; H, 4.05%. MS (m/e): M^+ 746(2), [$M^+ - 2\text{CO}$] 690(10), [$M^+ - 2\text{CO} - \text{MnCp}$] 570(7), [$M^+ - 4\text{CO} - \text{MnCp}$] 514(100), [$M^+ - 4\text{CO} - \text{MnCp}_2$] 449(5), [$M^+ - 4\text{CO} - \text{Mn}_2\text{Cp}_2$] 394(4), [$M^+ - 4\text{CO} - \text{PPh}_2$] 329(21), [$M^+ - 4\text{CO} - \text{PPh}_2\text{C}_2$] 305(12), [PPh_2C_2^+] 185(11), [MnCp^+] 120(28), [Mn^+] 55(30).

Preparation of **3** and **4**

Irradiation of $(\text{CO})_6\text{M}$ was performed as above (**3**: 2 g (9 mmol) $(\text{CO})_6\text{Cr}$, 300 ml THF, 5 h; **4**: 1 g (2.8 mmol) $(\text{CO})_6\text{W}$, 300 ml THF, 5 h). To the resulting solution of $(\text{CO})_5\text{MTHF}$ was added 2.4 g (6 mmol) or 0.8 g (2 mmol) DPPA. Stirring for 24 h yielded greenish-yellow solutions. The solvent was evaporated off at 20°C and

unchanged $(\text{CO})_6\text{M}$ was removed by sublimation as above. Crystallisation from pentane (3) or pentane/toluene (1/2) (4) yielded the products as pale yellow crystals.

3. Yield 2.3 g (62%), m.p. 117°C . Found: C, 56.58; H, 2.88. $\text{C}_{36}\text{H}_{20}\text{Cr}_2\text{O}_{10}\text{P}_2$ (778.50) calcd.: C, 55.54; H, 2.59%. MS (m/e): M^+ 778(5), $[M^+ - 3\text{CO}]$ 694(5), $[M^+ - 4\text{CO}]$ 666 (2.5), $[M^+ - 5\text{CO}]$ 638(45), $[M^+ - 6\text{CO}]$ 610(6), $[M^+ - 7\text{CO}]$ 582(5), $[M^+ - 8\text{CO}]$ 554(12), $[M^+ - 9\text{CO}]$ 526(13), $[M^+ - 10\text{CO}]$ 498(43), $[M^+ - 10\text{CO} - \text{Cr}]$ 446(100), $[M^+ - 10\text{CO} - 2\text{Cr}]$ 394(35), $[M^+ - 10\text{CO} - \text{CrPPh}_2]$ 261(18), $[\text{PPh}_2\text{C}_2^+]$ 209(78), $[\text{PPh}_2^+]$ 185(50), $[\text{Cr}^+]$ 52(90).

4. Yield 0.4 g (26%), m.p. 146°C . Found: C, 41.77; H, 1.80. $\text{C}_{36}\text{H}_{20}\text{W}_2\text{O}_{10}\text{P}_2$ (1042.21) calcd.: C, 41.48; H, 1.93%. MS (m/e): M^+ 1042(1.8), $[M^+ - 4\text{CO}]$ 930(1.1), $[M^+ - 5\text{CO}]$ 902(0.3), $[M^+ - 6\text{CO}]$ 874(1.1), $[M^+ - 7\text{CO}]$ 846(1.8), $[M^+ - 8\text{CO}]$ 818(0.6), $[M^+ - 9\text{CO}]$ 790(0.4), $[M^+ - 10\text{CO}]$ 762(1.3), $[M^+ - 6\text{CO} - \text{W}]$ 690(2.67), $[M^+ - 7\text{CO} - \text{W}]$ 662(0.4), $[M^+ - 8\text{CO} - \text{W}]$ 634(0.3), $[M^+ - 9\text{CO} - \text{W}]$ 606(1.0), $[M^+ - 10\text{CO} - \text{W}]$ 578(0.6), $[\text{PPh}_2\text{C}_2^+]$ 209(15), $[\text{PPh}_2^+]$ 185 (12), $[\text{W}^+]$ 184(10).

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