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PREPARATION OF η^2-ACETYLENE- AND η^1-VINYLIDENE-MANGANESE COMPLEXES FROM *p*-DIETHYNYLBENZENE AND CYMANTRENE. X-RAY CRYSTAL AND MOLECULAR STRUCTURE OF $Cp(OC)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$

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Summary

$Cp(OC)_2Mn(THF)$ reacts with *p*-diethynylbenzene (Deb), yielding $Cp(OC)_2$-$Mn(Deb)$ (I) and $[Cp(OC)_2Mn]_2(Deb)$ (II) with the η^2-acetylene coordination of Deb (to both Mn atoms in II). Under the action of PhLi, I and II are isomerized into $Cp(OC)_2Mn{=}C{=}CHC_6H_4C{\equiv}CH$ (III) and $[Cp(OC)_2Mn{=}C{=}CH]_2C_6H_4$ (VI). Treatment of I with PhLi, LiBr and an excess of HCl in ether, as well as direct interaction of III with LiBr and HCl/Et_2O, gives $Cp(OC)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$ (IV), which has been characterized by an X-ray single-crystal diffraction study. III adds PPh_3, yielding a zwitterionic complex, $Cp(OC)_2Mn^-{-}C(P^+Ph_3){=}CHC_6H_4C{\equiv}CH$ (V).

Introduction

The observation of π-acetylene-allenemetal rearrangement in the coordination sphere of the transition metal [1] initiated the preparation of various transition metal complexes with unsaturated carbene ligands [1–7]. However, all of these investigations were restricted to complexes with monoacetylene π-ligands. In the present work we attempted to expand this approach to *p*-diethynylbenzene (Deb), a diyne with isolated C≡C bonds, i.e. to coordinate Deb via both C≡C bonds and then to convert both π-acetylene moieties into metalallene moieties. Together with dimetal complexes, monometal complexes of both types were also prepared. Some of the complexes discussed below have been reported elsewhere [8].

Results and discussion

The interaction of equimolar amounts of $Cp(CO)_2Mn(THF)$ and Deb yields a mixture of products from which the mono- and di-manganese complexes I and II

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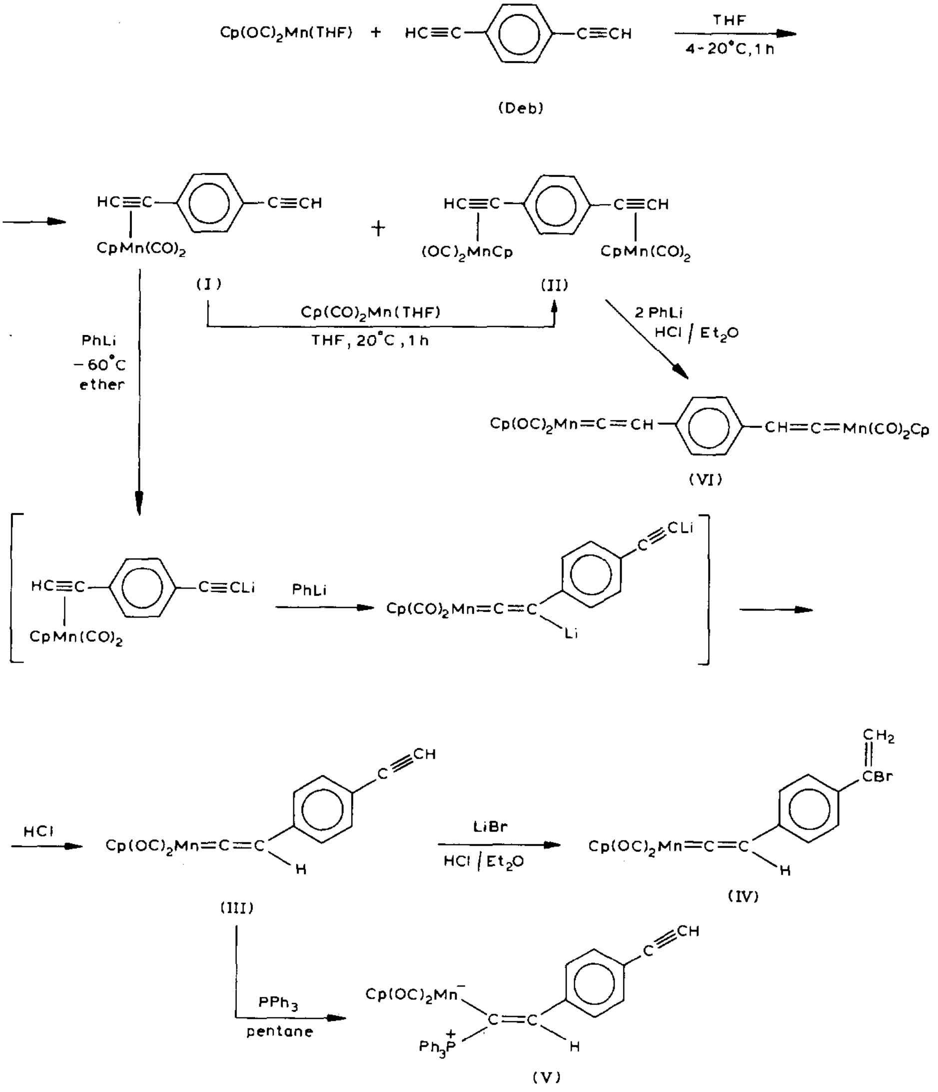

SCHEME 1. Cp = η^5-cyclopentadienyl.

(Scheme 1) were isolated by column chromatography. II is probably formed in a stepwise manner, i.e. an electron-deficient Cp(OC)$_2$Mn moiety adds to the uncoordinated C≡C bond of I. To confirm this assumption we performed the reaction between individual I and Cp(OC)$_2$Mn(THF) and obtained II with a 36% yield.

The yellow crystalline substances I and II are air-stable, unlike Cp(OC)$_2$Mn(η^2-HC≡CPh) [1]. I is readily soluble in most organic solvents; II is hardly soluble in aliphatic hydrocarbons and moderately soluble in CH$_2$Cl$_2$.

The IR spectra of I and II (CCl$_4$) show two ν(C≡O) bands at 1980, 1918 and 1995, 1930 cm^{-1}, respectively. The spectrum of I also shows the bands of an uncoordinated ethynyl moiety, viz. ν(C≡C) 2120 and ν(≡CH) 3310 cm^{-1}. The ν(C≡C) band of the coordinated ethynyl moiety in the spectra of I and II is shifted to 1840 cm^{-1}, i.e. to lower frequency with respect to the uncoordinated ethynyl. This effect is due to a decrease of the ethynyl C≡C bond order on coordination.

The ^{1}H NMR spectrum of I (CCl_4, TMS) shows signals of the protons of the Cp-ring, uncoordinated and coordinated ethynyl groups at δ 4.77, 3.03 and 5.40 ppm, respectively. Two doublets at δ 7.48 and 7.74 ppm correspond to two unequivalent pairs of benzene ring protons. The ^{1}H NMR spectrum of II ($CDCl_3$, TMS) shows singlets of the protons of the Cp ring and coordinated ethynyl at δ 4.73 and 5.49 ppm, while the benzene ring protons produce a singlet at δ 7.67 ppm.

Complex I, unlike $Cp(OC)_2Mn(\eta^2\text{-}HC{\equiv}CPh)$ [1], is not isomerized in the course of chromatography on Al_2O_3. Nevertheless, upon being treated with a double equivalent amount of PhLi and then with HCl (in ether), I rearranges into the (4-ethynyl)phenylvinylidene complex III (Scheme 1).

When the reaction mixture was treated with an excess of HCl in ether, we unexpectedly obtained, besides III, a product (IV) of HBr addition to the C≡C bond of III. We assumed that HBr was formed in the reaction mixture from HCl and an admixture of LiBr contained in the solution of phenyllithium (prepared from lithium and bromobenzene [9]). To confirm this assumption we treated III with LiBr and HCl in ether, and indeed obtained IV in a 28% yield.

Complex III (an air-unstable red oil) was characterized by IR and ^{1}H NMR spectroscopy. Its IR spectrum (CCl_4) shows two ν(C≡O) bands at 2010 and 1956 cm^{-1} and the ν(≡CH) band at 3316 cm^{-1}. The ^{1}H NMR spectrum of III (acetone-d_6, TMS) shows singlets of the protons of the Cp ring, ethynyl and vinylidene groups at δ 5.25, 3.53 and 5.75 ppm, respectively. The benzene ring protons give rise to two doublets at δ 7.12 and 7.33 ppm.

Elemental analysis of complex III was unsatisfactory because of its instability. However, III was characterized indirectly by a complete elemental analysis of its phosphonium derivative V, obtained by PPh_3 addition to the electron-deficient α-carbon atom of the vinylidene ligand (Scheme 1).

V is a bright red, crystalline, air-stable compound, practically insoluble in aliphatic hydrocarbons but moderately soluble in CH_2Cl_2, in which it dissociates into III and PPh_3.

The IR spectrum of V (in KBr) shows two ν(C≡O) bands at 1905 and 1830 cm^{-1}, i.e. shifted to lower frequencies relative to the bands of III, because the electron-donating PPh_3 moiety increases the electron density on the metal atom.

Complex IV, a red crystalline, air-stable substance, readily soluble in most organic solvents, was characterized by IR and ^{1}H NMR spectroscopy and an X-ray single-crystal diffraction study. Its IR spectrum (CCl_4) shows ν(C≡O) bands at 2014 and 1956 cm^{-1}, and the ^{1}H NMR spectrum (CCl_4, TMS) shows three singlets of equal intensity at δ 5.02, 6.01 and 6.58 ppm. By analogy with $PhBrC{=}CH_2$ ($\delta(CH_2)$ 5.75 and 6.08 ppm, J(HH) 2 Hz) [10], the signals at δ 5.02 and 6.01 ppm can be attributed to the $=CH_2$ group protons ($J(HH) \leqslant 3.4$ Hz) and the signal at δ 6.58 ppm, to the vinylidene proton. The cyclopentadienyl and benzene ring protons give rise to a singlet at δ 5.04 ppm and two doublets at δ 6.94 and 7.40 ppm.

The X-ray molecular structure of IV is shown in Fig. 1; bond distances and angles are listed in Table 1. The Mn atom has a "piano stool" coordination. The Mn=C(3) double bond length of 1.75(2) Å is somewhat smaller than the corresponding bond length 1.806 Å in $Cp(OC)_2Mn{=}C{=}C{=}C(C_6H_{11}\text{-cyclo})_2$ [11] and 1.79(2) Å in $(\eta^5\text{-}C_5H_4Me)(OC)_2Mn{=}C{=}CMe_2$ (VII) [12]. In $Cp(OC)_2Mn{=}C{=}CHPh$ (VIII) the Mn=C

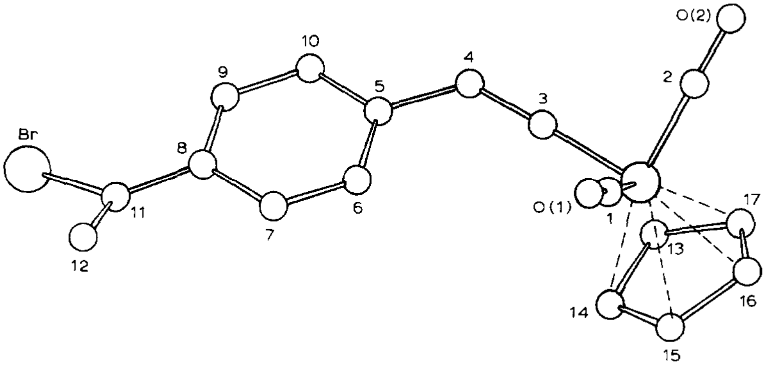

Fig. 1. Molecular structure of $Cp(OC)_2Mn{=}C{=}CHC_6H_4CBr{=}CH_2$ (IV) (the hydrogen atoms have been omitted).

bond is even shorter (1.68(2) Å) [13]. However, the accuracy of these structural determinations is not high enough to justify a discussion of these differences. The C(3) atom has a linear (*sp*) bond geometry with a bond angle of 177(2)°.

The C(3)=C(4) and C(11)=C(12) double bonds are inclined to the benzene ring plane at angles of 11° (vs. 10° in VIII) and 23°, respectively, probably because of intramolecular steric repulsion. The angle between the C(3)C(4)C(5) and Cp-ring planes is 32°, i.e. the p_π orbital of C(4) does not lie in the plane orthogonal to the Cp ring (as in VII) but is inclined to the latter (as in VIII). The Mn atom is 1.79 Å away from the Cp ring plane.

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) IN IV

Bond		Bond		Bond	
Mn–C(1)	1.80(3)	C(2)–O(2)	1.12(3)	C(8)–C(11)	1.44(3)
Mn–C(2)	1.77(2)	C(3)–C(4)	1.32(2)	C(11)–C(12)	1.30(3)
Mn–C(3)	1.75(2)	C(4)–C(5)	1.46(2)	C(11)–Br	1.90(2)
Mn–C(13)	2.12(3)	C(5)–C(6)	1.39(3)	C(13)–C(14)	1.45(4)
Mn–C(14)	2.18(3)	C(6)–C(7)	1.37(3)	C(14)–C(15)	1.39(3)
Mn–C(15)	2.18(2)	C(7)–C(8)	1.41(2)	C(15)–C(16)	1.39(4)
Mn–C(16)	2.12(2)	C(8)–C(9)	1.38(3)	C(16)–C(17)	1.28(4)
Mn–C(17)	2.11(3)	C(9)–C(10)	1.37(3)	C(17)–C(13)	1.37(4)
C(1)–O(1)	1.11(3)	C(10)–C(5)	1.39(2)		
Angle		**Angle**		**Angle**	
C(1)MnC(2)	90(1)	C(6)C(5)C(10)	116(2)	C(8)C(11)C(12)	131(2)
C(1)MnC(3)	90(1)	C(5)C(6)C(7)	123(2)	C(8)C(11)Br	117(1)
C(2)MnC(3)	91(1)	C(6)C(7)C(8)	121(2)	C(12)C(11)Br	112(2)
MnC(1)O(1)	177(2)	C(7)C(8)C(9)	116(2)	C(14)C(13)C(17)	107(2)
MnC(2)O(2)	178(2)	C(7)C(8)C(11)	119(2)	C(13)C(14)C(15)	105(2)
MnC(3)C(4)	177(2)	C(9)C(8)C(11)	125(2)	C(14)C(15)C(16)	107(2)
C(3)C(4)C(5)	128(2)	C(8)C(9)C(10)	122(2)	C(15)C(16)C(17)	112(2)
C(4)C(5)C(6)	122(2)	C(9)C(10)C(5)	121(2)	C(16)C(17)C(13)	110(2)
C(4)C(5)C(10)	121(2)				

The interaction of II with two equivalents of PhLi and then with HCl in ether gives bis-vinylidene complex VI in a 39.6% yield (Scheme 1). VI is a red crystalline, air-stable substance, poorly soluble in aliphatic hydrocarbons and moderately soluble in CH_2Cl_2.

The IR spectrum of VI (CH_2Cl_2) shows two $\nu(C\equiv O)$ bands at 2010 and 1950 cm^{-1}, i.e. shifted to lower frequencies by 15–20 cm^{-1} with respect to the parent complex II, due to the electron-accepting effect of the vinylidene ligand. The ^1H NMR spectrum of VI ($CDCl_3$, TMS) shows singlet signals at δ 5.04 (Cp), 6.64 ($=CH$) and 6.94 (C_6H_4) ppm. The equivalence of two pairs of CO groups in the IR spectrum, and of all the cyclopentadienyl, vinylidene and benzene protons in the NMR spectrum indicates that molecule VI is symmetrical.

Experimental

All reactions were performed under nitrogen, using absolute solvents saturated with nitrogen. Photochemical reactions were performed in a quartz Schlenk vessel with a water jacket using a PRK-7 mercury-quartz lamp (1000 W). For thin-layer chromatography, Al_2O_3 (Brockmann II, Reanal, Hungary) was employed. Commercial *p*-diethynylbenzene was recrystallized from hexane before use. Phenyllithium was prepared as described [9]. IR spectra were measured using a UR-20 Zeiss instrument and ^1H NMR spectra, with a Bruker WP 200 spectrometer (200 MHz). Mass spectra were measured using an MX-1303 mass spectrometer with a DS-50 data processing system (ionizing electron energy 70 eV, temperature of ion source 200°C, temperature of the injection system 20–50°C, direct injection).

An X-ray diffraction experiment was performed at room temperature with a Hilger & Watts four-circle autodiffractometer (graphite-monochromated Mo-K_α radiation). All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [14].

Crystal data: orthorhombic, space group $P2_12_12_1$, a 6.925(1), b 8.559(1), c 26.589(2) Å, V 1575.9(2) Å^3, $Z = 4$. $C_{17}H_{12}BrMnO_2$, d_{calcd} 1.62 g cm^{-3}, μ(Mo-K_α) 35.6 cm^{-1}.

The intensities of 889 independent reflections (without Friedel equivalents) with $I \geqslant 2\sigma$ were measured by $\theta/2\theta$ scan mode ($\theta \leqslant 25°$). The structure was solved by Patterson and Fourier methods. Block diagonal least-squares refinement (Br and Mn atoms anisotropic, with anomalous scattering corrections; C and O isotropic) converged to $R = 0.085$ vs. $R = 0.091$ for the enantiomorphic structure. According to the Hamilton R-factor ratio test [15], the former absolute structure is true at the 99.5% significance level. Further full matrix refinement involving all the hydrogen atoms as fixed contributions (in calculated positions, B_{iso} 10 Å^2 for cyclopentadienyl hydrogens, B_{iso} 6 Å^2 for the others) converged to $R = 0.073$ (vs. $R = 0.082$ for the enantiomorphic structure). A unit weighting scheme was used. The final positional and thermal atomic parameters are listed in Table 2.

Reaction of Cp(OC)$_2$Mn(THF) with Deb

Deb (0.8 g, 6.34 mmol) was added to a solution of $Cp(OC)_2Mn(THF)$, prepared by UV irradiation (2 h exposure at 4°C) of cymantrene (3.0 g, 14.7 mmol), dissolved in THF (180 ml). The mixture was stirred for 30–40 min at 4–20°C, the solvent was removed in vacuo, and the residue was extracted with hexane (8–9 times × 15 ml)

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) AND ANISOTROPIC THERMAL FACTORS $T=\exp[-1/4(B_{11}h^2a^{*2}+\ldots 2B_{12}hka^*b^*+\ldots)]$ IN IV

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	8283(4)	9318(4)	9246(1)	5.0(1)	4.2(1)	4.6(1)	0.2(2)	0.0(1)	−0.6(1)
Br	15681(4)	9329(4)	6300(1)	9.0(2)	11.7(2)	6.9(1)	1.7(2)	2.0(1)	3.8(2)
Atom	x	y	z	B_{iso} (Å^2)	Atom	x	y	z	B_{iso} (Å^2)
O(1)	9505(25)	6065(21)	9260(6)	8.7(4)	O(2)	4333(27)	8243(20)	9195(6)	8.6(4)
C(1)	9080(38)	7317(29)	9252(9)	6.8(6)	C(2)	5855(34)	8692(25)	9211(8)	6.1(5)
C(3)	8477(26)	9346(25)	8590(6)	4.7(4)	C(4)	8620(26)	9460(24)	8096(6)	4.7(4)
C(5)	10278(23)	9072(20)	7783(5)	3.7(3)	C(6)	11905(28)	8325(21)	7974(6)	4.4(4)
C(7)	13477(28)	7980(21)	7683(6)	4.3(4)	C(8)	13561(27)	8466(21)	7176(6)	4.1(4)
C(9)	11955(26)	9226(25)	6991(6)	4.8(4)	C(10)	10348(26)	9505(23)	7280(6)	4.7(4)
C(11)	15263(29)	8117(24)	6886(7)	5.1(4)	C(12)	16540(32)	7019(24)	6935(7)	5.7(5)
C(13)	8738(40)	11753(29)	9343(9)	7.6(7)	C(14)	10581(38)	10987(29)	9410(8)	7.7(6)
C(15)	10344(37)	10009(28)	9825(8)	7.5(6)	C(16)	8456(38)	10206(29)	9987(9)	7.4(6)
C(17)	7549(43)	11210(34)	9717(10)	9.3(8)					

until it no longer coloured the solvent. The hexane extracts were combined, the solvent was removed in vacuo, and the residue was chromatographed on an Al_2O_3 column at 10°C, using petroleum ether/CH_2Cl_2 (3/1) as eluant. A yellow zone yielded cymantrene (2.25 g, 75%) and a yellow-orange zone yielded yellow crystalline I (0.62 g, 55% to the reacted cymantrene), m.p. 98–100°C (dec.). Found: C, 67.66; H, 3.79; Mn, 17.93%. $C_{17}H_{11}MnO_2$ calcd.: C, 67.56; H, 3.67; Mn, 18.18%. The residue remaining after extraction with hexane was dissolved in CH_2Cl_2, the solution was filtered, and the solvent removed in vacuo, yielding yellow crystalline II (0.20 g, 22.7% to the reacted cymantrene), m.p. 131–135°C (dec.). Found: C, 59.86; H, 3.31; Mn, 22.35. $C_{24}H_{16}Mn_2O_4$ calcd.: C, 60.28; H, 3.57; Mn, 22.98%.

Preparation of II

I (1.07 g, 3.54 mmol) was added to a solution of $Cp(OC)_2Mn(THF)$, prepared by UV irradiation (2 h exposure at 4°C) of the cymantrene (3.0 g, 14.7 mmol) solution in THF (150 ml). The mixture was stirred for 3 h at 4–20°C. The solvent was removed in vacuo, the residue was washed with petroleum ether (6×10 ml) and recrystallized from CH_2Cl_2, yielding II (0.61 g, 36% to the reacted I), which was identified by IR and ^1H NMR spectroscopy. The petroleum ether extracts were combined, the solvent was removed in vacuo, and the residue was chromatographed on Al_2O_3 at 10°C. Cymantrene (2.0 g) and unreacted I (0.49 g) were eluted by petroleum ether/CH_2Cl_2 (3/1). I was identified by IR spectroscopy.

Preparation of III

A 0.7 *N* ether solution of PhLi (7.8 ml) was added at −60°C to I (0.82 g, 2.71 mmol) dissolved in ether (40 ml). A yellow-orange precipitate formed. The mixture was stirred for 10–15 min at −55°C, then 1.5 ml of 3.5 *N* HCl/Et_2O solution was added. The precipitate dissolved and the solution changed from yellow-orange to a light red colour. The mixture was warmed to 20°C (at 5–10°C, white LiCl precipitated), the solvent was removed in vacuo, and the residue was chromatographed on

Al_2O_3. A red zone eluted with petroleum ether/CH_2Cl_2 (4/1) yielded III (0.58 g, 71%) as a red oil, unstable to air.

Reaction of I with PhLi and an excess of HCl

0.7 *N* ether solution of PhLi (6.24 ml) was added to I (0.66 g, 2.18 mmol) dissolved in 40 ml of ether at −60°C. The mixture was stirred for 15 min at −55 to −60°C, then 2.1 ml of 3.5 *N* ether solution of HCl was added. The mixture changed from dark orange to a blue-green colour. It was then warmed to 20°C, the solvent was removed in vacuo, and the residue was chromatographed on Al_2O_3 at 10°C. A red zone eluted with petroleum ether/CH_2Cl_2 (4/1) yielded IV (0.19 g, 22.89%) as light-red crystals, m.p. 80–81°C (dec.). Found: C, 54.02; H, 3.38; Mn, 15.00. $C_{17}H_{12}BrMnO_2$ calcd.: C, 53.30; H, 3.15; Mn, 14.33%. Another red zone eluted with the same solvent yielded III (0.21 g, 31.82%), identified by its IR and ^1H NMR spectra.

Preparation of IV from III and LiBr

Anhydrous LiBr (1.0 g, 11.5 mmol) in ether (35 ml) and 3.56 *N* HCl/Et_2O solution (1.5 ml, 5.34 mmol) were added to III (0.36 g, 1.19 mmol). The mixture changed from light red to a black blue colour and a black-blue precipitate formed. The mixture was stirred for 15 min at 20°C and neutralized with 15 ml of 10% aqueous Na_2CO_3 solution. The light-red ether layer was separated from the light-yellow aqueous one, and washed with water. The solvent was removed in vacuo and the residue was chromatographed on Al_2O_3. A red zone eluted with petroleum ether/CH_2Cl_2 (4/1) yielded IV (0.13 g, 28%), identified by m.p. and IR spectrum.

Reaction of III with PPh_3

PPh_3 (0.26 g, 1.00 mmol) in pentane (15 ml) was added to III (0.1 g, 0.33 mmol) in pentane (15 ml). The mixture was refluxed for 30 min and concentrated in vacuo to two thirds of the starting volume. A red precipitate formed. The solution was decanted, the precipitate washed with pentane (6 × 3 ml) and dried in vacuo, yielding red crystalline, air-stable V (0.12 g, 64.5%), m.p. 100–120°C (dec.). Found: C, 74.61; H, 4.70; P, 5.39. $C_{29}H_{22}MnO_2P$ calcd.: C, 74.47; H, 4.64; P, 5.49%. Mass spectrum (*m/z*): 302 $[M - PPh_3]^+$, 246 $[M - PPh_3 - 2CO]^+$, 126 $[C_2HC_6H_4C{\equiv}CH]^+$.

Preparation of VI

0.7 *N* ether solution of PhLi (3.46 ml) was added at −65°C to a suspension of II (0.58 g, 1.21 mmol) in ether (50 ml). Thereafter the precipitate of II dissolved, and the solution became dark red. After stirring for 30 min, the mixture was allowed to warm from −65 to −30°C. Then 1 ml of 3.5 *N* HCl/Et_2O solution was added. The mixture was warmed to 20°C, the solvent was removed in vacuo, and the residue was chromatographed on Al_2O_3. A red zone eluted with petroleum ether/CH_2Cl_2 (2/1) yielded red crystalline, air-stable VI (0.23 g, 39.6%), m.p. 160°C (dec.). Found: C, 60.21; H, 3.58; Mn, 22.35. $C_{24}H_{16}Mn_2O$ calcd.: C, 60.28; H, 3.37; Mn, 22.98%.

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