*Organometallics* **1993,** *12,* 397-407

# Orthomanganated Arenes in Synthesis. 9. Photochemical Reactions of Alkynes with Orthomanganated Triphenyl Phosphite

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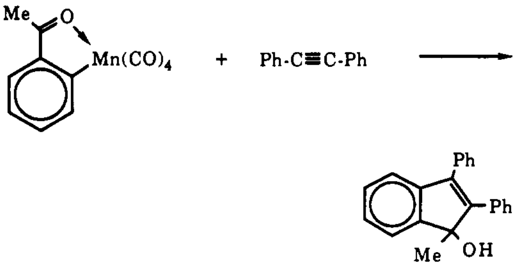
*Received August 10, 1992*

The reaction of orthomanganated triphenyl phosphite, $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (1), with alkynes ($C_2Ph_2$, $C_2(COOMe)_2$, PhCCH, $Me_3SiCCH$) under UV irradiation gives products derived from insertion of the alkyne into the Mn–C bond. The main products are the seven-membered metallacyclic species $(PhO)_2P(OC_6H_4)C(R^2){=}C(R^1)Mn(CO)_4$ (2) (both regioisomers for the unsymmetrical alkynes). Also obtained from the $C_2Ph_2$ reaction was $(PhO)_2POC_6H_4)C(Ph){=}C(Ph)C(O)Mn(CO)_3$ (4), formed by insertion of both $C_2Ph_2$ and CO, and a compound $\{2,6\text{-}[PhCH{=}C(Ph)]_2C_6H_3O\}\{2\text{-}[PhCH{=}C(Ph)]C_6H_4O\}POC_6H_4)Mn(CO)_4$ (3) derived from 1 by substitution with $-C(Ph){=}C(Ph)H$ groups at three of the ortho sites on the unmetalated phenoxy rings by a sequence of insertion/demetalation steps. A metal acetylide, $PhCCMn(CO)_3[P(OPh)_3]_2$ (6) was also isolated from the reaction with PhCCH. Crystal structures are described for **2e** ($R^1$ = Ph, $R^2$ = H; triclinic, space group $P\bar{1}$, $a$ = 10.619 (11) Å, $b$ = 10.896 (6) Å, $c$ = 11.619 (8) Å, $\alpha$ = 77.68 (5)°, $\beta$ = 80.81 (7)°, $\gamma$ = 80.31 (6)°, $Z$ = 2, 2772 reflections, $R$ = 0.039), **3** (monoclinic, space group $P2_1/n$, $a$ = 10.743 (6) Å, $b$ = 27.456 (23) Å, $c$ = 17.536 (14) Å, $\beta$ = 104.86 (5)°, $Z$ = 4, 3941 reflections, $R$ = 0.0599), **4** (monoclinic, space group $P2_1/n$, $a$ = 9.907 (6) Å, $b$ = 18.458 (11) Å, $c$ = 16.539 (8) Å, $\beta$ = 94.35 (4)°, $Z$ = 4, 2565 reflections, $R$ = 0.104), and **6** (orthorhombic, space group $P2_12_12_1$, $a$ = 19.888 (6) Å, $b$ = 19.732 (8) Å, $c$ = 10.467 (4) Å, $Z$ = 4, 3085 reflections, $R$ = 0.0523).

## Introduction

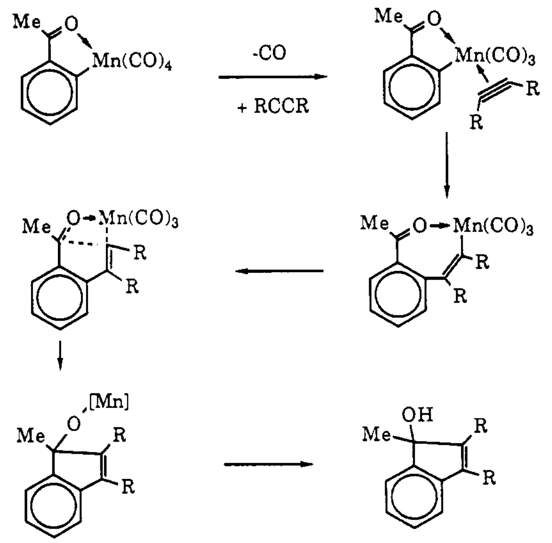
Alkynes undergo cycloaddition reactions with orthomanganated aryl ketones.[1-3] For example, orthomanganated acetophenone with alkynes gives inden-1-ols, eq 1.



(1)

The reaction can be initiated either by thermal means[1] or with trimethylamine $N$-oxide.[2] Although a reasonable reaction sequence can be proposed[1,2] (Scheme I), none of the suggested intermediates in the reactions with ketones has been detected. In searching for related systems where parallel reactions might provide precedents, we noted a report[4] that the photochemical reaction of orthomanganated triphenyl phosphite[5] (1) with $C_2Ph_2$ gave an $\eta^2$-alkyne complex. This was later shown to be in error,[6] and the main compound formed was in fact **2a**, a seven-membered metallacyclic compound formed by insertion of the alkyne into the Mn–C bond. Alkyne insertion reactions are well-known for other metal complexes,[7] but in contrast to the wealth of information relating to the CO-insertion reactions of manganese alkyls, there have

**Scheme I**



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0276-7333/93/2312-0397$04.00/0

been few studies of alkyne insertion into Mn–C bonds. The only examples that we are aware of involve the formation of cyclometalated enones from alkynes and alkyl manganese pentacarbonyls.[8] We have therefore characterized some of the other products from the $C_2Ph_2$ system and have examined the reactions of other alkynes with 1.

## Experimental Section

All air-sensitive reactions were performed under an atmosphere of dry nitrogen using Schlenk techniques, with dried, $N_2$-saturated solvents. Photochemical reactions were performed in a 200-mL reaction vessel into which a Hanovia 125-W water-cooled medium-pressure mercury lamp (fitted with a quartz sleeve) was inserted. Unless otherwise indicated, infrared spectra were recorded on a Digilab FTS-45 FTIR as solutions in $CH_2Cl_2$, while $^1$H and $^{13}$C NMR spectra were recorded (as $CDCl_3$ solutions) on either a JEOL FX-90Q or Bruker AC300 instrument and $^{31}$P NMR spectra ($CDCl_3$) were recorded on a JEOL FX-90Q instrument, referenced to 85% $H_3PO_4$ using the low-field-positive convention. FAB mass spectra were obtained at the University of Adelaide on a VG ZAB 2HF instrument. Chromatographic separations were performed on silica gel plates (Merck Kieselgel 60). Elemental analyses were performed by the University of Otago Microanalytical Laboratory. $PhCH_2Mn(CO)_5$ was prepared by the standard method.[9]

**Preparation of Orthomanganated Triphenyl Phosphite (1).** This was prepared by a variation of the method of Kaesz et al.[5] $PhCH_2Mn(CO)_5$ (2.54 g, 8.88 mmol) and $P(OPh)_3$ (2.75 g, 8.88 mmol) were dissolved in dry thf (180 mL), and the flask was evacuated and then purged with $N_2$. The solution was refluxed for 4.5 h, the reaction progress being monitored by both tlc and IR. The solvent was removed under vacuum to yield, as a yellow oil, $PhCH_2Mn(CO)_4P(OPh)_3$ [IR (thf), $\nu$(CO) 2068 (s), 2001 (s, br), 1978 (vs, br), 1960 (s, br) cm$^{-1}$].[5] Without further purification, this yellow oil was dissolved in toluene (170 mL) and the solution was refluxed for 2 h. The solvent was removed under vacuum, and the residual oil was chromatographed, eluting with $CH_2Cl_2$/petroleum ether (1:9) to give three bands.

*Band 1* ($R_f$ = 0.68) was identified by IR as $Mn_2(CO)_{10}$ (0.17 g, 5%). *Band 2* ($R_f$ = 0.26) was orthomanganated triphenyl phosphite, $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_4$ (1), as a yellow oil (2.60 g, 61%): IR $\nu$(CO) 2083 (s), 1998 (s, br), 1971 (s, br) cm$^{-1}$; $^1$H NMR $\delta$ 7.23 (m) (10 H, Ar–H), 7.02 (m) (4 H, Ar–H); $^{31}$P NMR $\delta$ 193.0 (lit.[5] $\delta$ 193.1). *Band 3* ($R_f$ = 0.13) was recrystallized from $CH_2Cl_2$/petroleum ether (1:12) to yield fine yellow plates of the substituted analogue of 1, $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_3P(OPh)_3$ (1.10 g, 16%): IR $\nu$(CO) 2033 (s), 1974 (s, br), 1946 (s, br) cm$^{-1}$; $^{31}$P NMR $\delta$ 194.0 (d, $J_{pp}$ = 102 Hz), 157.4 (d, $J_{pp}$ = 102 Hz).

**Reaction of $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_4$ (1) with $C_2Ph_2$.** A solution of $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_4$ (1) (1.355 g, 2.85 mmol) and $C_2Ph_2$ (0.71 g, 3.99 mmol) in benzene (150 mL) was purged with $N_2$. The solution was irradiated with UV light for 18 h under a $N_2$ atmosphere at ambient temperature. The solvent was removed under vacuum to leave a yellow-brown oil, which was chromatographed, eluting with $CH_2Cl_2$/petroleum ether (1:4). This resulted in nine bands. *Band 1* ($R_f$ = 0.90) was $C_2Ph_2$. *Band 2* ($R_f$ = 0.80) was unreacted 1. *Band 3* ($R_f$ = 0.60) was recrystallized from diethyl ether/pentane at 4 °C to yield white block-shaped crystals of 3 (ca. 1%): mp 195 °C; IR $\nu$(CO) 2083 (s), 2000 (s, br), 1967 (s) cm$^{-1}$; $^1$H NMR $\delta$ 7.85 (d), 7.75 (d), 7.30 (s), 7.26 (s), 7.17 (s), 7.07 (s), 6.93 (d), 6.62 (d), 6.53 (s), 6.42 (s); $^{13}$C NMR $\delta$ 142.3 (s), 132.2 (d), 132.0 (d), 131.1 (d), 130.0 (d), 129.9 (d), 129.8 (d), 129.7 (d), 128.4 (d), 128.2 (d), 128.0 (d), 127.8 (d), 127.7 (d), 127.2 (d), 127.0 (d), 126.8 (d), 125.6 (d), 123.8 (d), 114.2 (s); $^{31}$P NMR $\delta$ 193.3; FAB MS $m/e$ 954 [M – 2CO]$^+$, 926 [M – 3CO]$^+$, 898 [M – 4CO]$^+$, 844 [M – Mn(CO)$_4$]$^+$, 805 [M – 4CO – OPh]$^+$, 627 [M – 4CO – $C_2Ph_2$ – OPh]$^+$, 504 [M – 4CO – P(OPh)$_2$ – $C_2Ph_2$]$^+$, 325 [M – 4CO – P(OPh)$_2$ – 2$C_2Ph_2$]$^+$. This compound was further characterized by X-ray crystallography (see below).

*Band 4* ($R_f$ = 0.45) was recrystallized from cyclohexane/petroleum ether to give white needle-shaped crystals of $(PhO)_2\overline{P(OC_6H_4)C(Ph){=}C(Ph)Mn}(CO)_4$ (**2a**) (0.295 g, 15%): mp 148–150 °C; IR $\nu$(CO) 2079 (s), 2009 (s), 1992 (vs, br), 1969 (s) cm$^{-1}$; $^1$H NMR $\delta$ 7.38 (m), 7.14 (m), 6.92 (m); $^{13}$C NMR $\delta$ 157.7 (d), 152.2 (s), 149.3 (s), 147.2 (s), 145.9 (s), 139.9 (d), 134.0 (d), 131.2 (d), 130.7 (d), 129.0 (d), 127.8 (d), 126.0 (d), 125.7 (d), 124.2 (d), 122.0 (d); $^{31}$P NMR $\delta$ 171.8 (s); FAB MS $m/e$ 654 [M]$^+$ 542 [M – 4CO]$^+$ (base peak), 488 [M – Mn(CO)$_4$]$^+$, 449 [M – 4CO – OPh]$^+$, 364 [M – 4CO – $C_2Ph_2$]$^+$. The X-ray crystal structure of this compound has been reported elsewhere.[6]

*Band 5* ($R_f$ = 0.31) was recrystallized from $CH_2Cl_2$/petroleum ether (1:10) to give yellow crystals of $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_3P(OPh)_3$ (0.025 g, 1%), identified by IR and $^{31}$P NMR spectroscopy.

*Band 6* ($R_f$ = 0.25) was recrystallized from diethyl ether/pentane at 4 °C to give dark brown, platelike crystals (0.066 g), which were not identified: mp 196 °C; IR $\nu$(CO) 1966 (vs), 1918 (s) cm$^{-1}$; $^1$H NMR $\delta$ 7.01 (m); $^{13}$C NMR $\delta$ 138.5 (s), 132.5 (s), 132.1 (d), 131.6 (d), 130.1 (d), 128.3 (d), 124.9 (d), 122.5 (d), 121.8 (d); $^{31}$P NMR $\delta$ 214.3 (s); FAB MS $m/e$ 1030, 928, 853, 720 (base peak), 674, 628, 542, 504, 466.

*Band 7* ($R_f$ = 0.22) was recrystallized from $CH_2Cl_2$/petroleum ether (1:10) to give pale orange crystals of $(PhO)_2\overline{P(OC_6H_4)C(Ph){=}C(Ph)Mn}(CO)_3P(OPh)_3$, the $P(OPh)_3$ derivative of **2a** (0.009 g, 0.3%). Anal. Calcd for $C_{53}H_{39}MnO_9P_2$: C, 67.95; H, 4.20. Found: C, 68.27; H, 4.17. Mp: 140 °C. IR: $\nu$(CO) 2048 (s), 1971 (vs), 1946 (s) cm$^{-1}$. $^1$H NMR: $\delta$ 7.23 (m). $^{31}$P NMR: $\delta$ 175.2 (d) ($J_{pp}$ = 169 Hz), 163.8 (d) ($J_{pp}$ = 169 Hz). FAB MS: $m/e$ 852 [M – 3CO]$^+$, 759 [M – 3CO – OPh]$^+$, 674 [M – 3CO – $C_2Ph_2$]$^+$, 666 [M – 3CO – 2OPh)$^+$, 542 [M – 3CO – P(OPh)$_3$]$^+$ (base peak), 488 [M – Mn(CO)$_3$P(OPh)$_3$]$^+$.

*Band 8* ($R_f$ = 0.19) was recrystallized from $CH_2Cl_2$/petroleum ether (1:9) to give well-formed chunky red-orange crystals of $(PhO)_2\overline{P(OC_6H_4)C(Ph){=}C(Ph)C(O)Mn}(CO)_3$ (4) (0.113 g, 6%): mp 152–153 °C; IR $\nu$(CO) 2037 (vs), 1987 (s), 1952 (s, br), 1793 (w, br) cm$^{-1}$; $^1$H NMR $\delta$ 7.19 (m), 6.81 (m); $^{13}$C NMR $\delta$ 151.8 (s), 151.6 (s), 151.4 (s), 151.0 (s), 150.8 (s), 149.4 (s), 134.4 (d), 133.6 (d), 130.8 (d), 130.3 (d), 129.6 (d), 129.3 (d), 128.6 (d), 128.4 (d), 127.5 (d), 126.0 (d), 125.3 (d), 121.9 (d), 121.2 (d); $^{31}$P NMR $\delta$ 166.4 (s); FAB MS $m/e$ 626 [M – CO]$^+$, 598 [M – 2CO]$^+$, 570 [M – 3CO]$^+$, 542 [M – 4CO]$^+$ (base peak), 488 [M – Mn(CO)$_4$]$^+$, 449 [M – 4CO – OPh]$^+$. This compound was further characterized by X-ray crystallography.

*Band 9* ($R_f$ = 0.09) was an unidentified orange oil (0.084 g) which did not crystallize: IR $\nu$(CO) 2085 (w), 2002 (s, br), 1938 (m, br) cm$^{-1}$; FAB MS $m/e$ 531 (base peak) 392, 327.

**Reaction of $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_4$ (1) with $C_2(COOMe)_2$.** 1 (1.342 g, 2.82 mmol) and dimethyl acetylenedicarboxylate, DMAD (0.79 g, 5.56 mmol), were dissolved in benzene (150 mL), and the solution was irradiated under $N_2$ for 18 h. The solvent was removed under vacuum to leave a yellow-brown oil. The oil was chromatographed with $CH_2Cl_2$/petroleum ether (1:2) to yield five bands. *Band 1* was unreacted 1 ($R_f$ = 0.71) and *band 2* ($R_f$ = 0.50) was unreacted alkyne. *Band 3* ($R_f$ = 0.36) was a yellow oil which was recrystallized from $CH_2Cl_2$/petroleum ether (1:4) to give white crystals of

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$(PhO)_2P(OC_6H_4)C(COOMe){=}C(COOMe)Mn(CO)_4$ (**2b**) (0.787 g, 45%). Mp: 138–140 °C. Anal. Calcd for $C_{28}H_{11}MnO_{11}P$: C, 54.39; H, 3.26. Found: C, 54.42; H, 3.39. IR: ν(CO) 2090 (s), 2032 (s), 2005 (vs), 1989 (s), 1712 (s) cm$^{-1}$. $^1$H NMR: δ 7.25 (m, 14 H, Ar—H), 3.81 (s, 3 H, $COOCH_3$), 3.66 (s, 3 H, $COOCH_3$). $^{13}$C NMR: δ 163.3 (s), 150.4 (s), 147.2 (s), 142.0 (d), 132.0 (d), 131.9 (d), 129.2 (d), 129.0 (d), 124.7 (d), 121.1 (d), 120.1 (d), 120.0 (d), 52.5 (q) ($OCH_3$), 51.5 (q) ($OCH_3$). $^{31}$P NMR: δ 172.3. FAB MS: *m/e* 590 [M − CO]$^+$, 534 [M − 3CO]$^+$, 506 [M − 4CO]$^+$ (base peak), 476 [M − DMAD]$^+$, 448 [M − DMAD − CO]$^+$, 420 [M − DMAD − 2CO]$^+$, 413 [M − 4CO − OPh]$^+$.

*Band 4* ($R_f$ = 0.25) was $(PhO)_2P(OC_6H_4C(COOMe){=}C(COOMe)Mn(CO)_3P(OPh)_3$, the $P(OPh)_3$ derivative of **2b**, as a yellow oil (0.0091 g, 0.4%), identified spectroscopically: IR ν(CO) 2047 (s), 2011 (s), 1982 (m) cm$^{-1}$; $^1$H NMR δ 7.25 (m, 29 H, Ar—H), 3.78 (s, 3 H, $COOCH_3$), 3.68 (s, 3 H, $COOCH_3$).

*Band 5* ($R_f$ = 0.18) gave $(PhO)_2P(OC_6H_4)C(R){=}C(R)C(R){=}C(R)Mn(CO)_4$, R = COOMe (**5**), as yellow crystals (0.258 g, 12%). Mp: 79–80 °C. Anal. Calcd for $C_{34}H_{26}MnO_{15}P$: C, 53.70; H, 3.45. Found: C, 54.42; H, 3.39. IR: ν(CO) 2091 (s), 2035 (m), 2004 (s, br), 1989 (s), 1931 (m, br), 1712 (s) cm$^{-1}$. $^1$H NMR: δ 7.27 (m, 14 H, Ar—H), 3.86 (s, 6 H, $COOCH_3$), 3.54 (s, 3 H, $COOCH_3$), 3.47 (s, 3 H, $COOCH_3$). $^{31}$P NMR ($CDCl_3$): δ 146.8. FAB MS: *m/e* 648 [M − 4CO]$^+$ (base peak) 618 [M − DMAD]$^+$, 555 [M − 4CO − OPh]$^+$, 506 [M − 4CO − DMAD]$^+$.

**Reaction of $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (1) with $Me_3SiCCH$.** $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (1) (0.781 g, 1.64 mmol) and $Me_3SiCCH$ (0.406 g, 4.14 mmol) were dissolved in benzene (100 mL), and the solution was irradiated for 22 h under $N_2$. The solvent was removed under vacuum to give a dark red oil which was chromatographed using $CH_2Cl_2$/petroleum ether (1:9) to give three major bands.

*Band 1* ($R_f$ = 0.88) was a yellow oil, recrystallized from $CH_2Cl_2$/petroleum ether (1:10), to give colorless crystals of $(PhO)_2P(OC_6H_4)CH{=}C(SiMe_3)Mn(CO)_4)$ (**2c**) (0.103 g, 11%). Mp: 202–203 °C. Anal. Calcd for $C_{27}H_{24}MnO_7PSi$: C, 56.45; H, 4.21. Found: C, 56.21; H, 4.46. IR: ν(CO) 2078 (s), 2010 (s), 1990 (vs, br), 1969 (s) cm$^{-1}$. $^1$H NMR: δ 7.37–7.10 (m, 14 H), 6.90 (d, *J* = 7.9 Hz, 1 H), 6.60 (d, *J* = 5.5 Hz, 1 H), −0.12 (s, 9 H). $^{13}$C NMR: δ 212.7 (CO), 210.2 (CO), 167.7 ($J_{P-C}$ = 35.5 Hz), 154.3 (s, $J_{P-C}$ = 4.6 Hz), 145.3 (s, $J_{P-C}$ = 8.7 Hz), 129.8 (d), 128.4 (s, $J_{P-C}$ = 8.9 Hz), 127.5 (d), 125.4 (d), 124.8 (d, $J_{P-C}$ = 1.5 Hz), 124.0 (d), 121.3 (d), 118.6 (d, $J_{P=C}$ = 5.1 Hz), 0.6 (q, Si$CH_3$). $^{31}$P NMR: δ 176.8. FAB MS: *m/e* 559 [M − Me]$^+$, 462 [M − 4CO]$^+$, 369 [M − 4CO − OPh]$^+$.

*Band 2* ($R_f$ = 0.78) was recovered starting material (1) (0.204 g, 26% recovered).

*Band 3* ($R_f$ = 0.68) was a pale-orange oil, identified as $(PhO)_2P(OC_6H_4)C(SiMe_3){=}C(H)Mn(CO)_4$ (**2d**) (0.107 g, 11%) which could not be crystallized: IR ν (CO) 2098 (s), 2026 (s), 2012 (vs, br), 1985 (s) cm$^{-1}$; $^1$H NMR δ 7.38 (m), 7.35 (m), 7.33 (m), 7.27 (m), 7.22 (m), 7.19 (m, 15 H, Ar—H), 0.16 (s, 9 H, Si$CH_3$); $^{13}$C NMR δ 152.2 (d), 130.5 (s), 126.5 (s), 122.2 (s), 1.8 (s, 3 C, Si$CH_3$); $^{31}$P NMR δ 156.5 (s); FAB MS *m/e* 462 [M − 4CO]$^+$ (base peak), 476 [M − $Me_3SiCCH$]$^+$, 369 [M − 4CO − OPh]$^+$.

**Reaction of $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (1) with PhCCH.** 1 (1.239 g, 2.60 mmol) and PhCCH (0.278 g, 2.72 mmol) were dissolved in benzene (150 mL), and the solution was irradiated for 18 h under $N_2$. The solvent was removed under vacuum to leave a red oil which was chromatographed with $CH_2Cl_2$/petroleum ether (1:3) to produce six bands.

*Band 1* ($R_f$ = 0.90) was unreacted 1 (0.354 g, 28% recovered).

*Band 2* ($R_f$ = 0.85) was recrystallized from $CH_2Cl_2$/pentane at 4 °C to give white block-shaped crystals of $(PhO)_2P(OC_6H_4)CH{=}C(Ph)Mn(CO)_4$ (**2e**) (0.202 g, 13%). Mp: 110 °C. Anal. Calcd for $C_{30}H_{20}MnO_7P$: C, 62.30; H, 3.49. Found: C, 62.50; H, 3.50. IR: ν(CO) 2081 (s), 2013 (s), 1995 (vs), 1975 (s) cm$^{-1}$. $^1$H NMR: δ 7.32–6.68 (m). $^{13}$C NMR δ 159.3 (s), 152.2 (s), 151.7 (s), 142.9 (s), 138.3 (s), 134.4 (s), 132.3 (d), 130.6 (d), 128.5 (d), 128.3 (d), 125.9 (d), 125.2 (d), 121.9 (d), 121.7 (d). $^{31}$P NMR: δ 166.7 (s). FAB MS: *m/e* 494 [M − 3CO]$^+$, 466 [M − 4CO]$^+$ (base peak), 411, 373 [M − 4CO − OPh]$^+$. This compound was further characterized by X-ray crystallography (see below).

*Band 3* ($R_f$ = 0.56) was a yellow oil of $(PhO)_2P(OC_6H_4)C(Ph){=}C(H)Mn(CO)_4$ (**2f**) (0.132 g, 8%) which did not crystallize: IR ν(CO) 2090 (s), 2030 (s), 2015 (vs), 1985

**Table I. X-ray Crystal Structure Details**

| | **2e** | **3** | **4** | **6** |
|---|---|---|---|---|
| formula | $C_{30}H_{20}MnO_7P$ | $C_{64}H_{44}MnO_7P$ | $C_{36}H_{24}MnO_7P$ | $C_{47}H_{35}MnO_9P_2$ |
| $M_r$, g mol$^{-1}$ | 578.4 | 1010.97 | 654.5 | 860.68 |
| cryst syst | triclinic | monoclinic | monoclinic | orthorhombic |
| space group | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ | $P2_12_12_1$ |
| *a*, Å | 10.619 (11) | 10.743 (6) | 9.907 (6) | 19.888 (6) |
| *b*, Å | 10.896 (6) | 27.456 (23) | 18.458 (11) | 19.732 (8) |
| *c*, Å | 11.619 (8) | 17.536 (14) | 16.539 (8) | 10.467 (4) |
| α, deg | 77.68 (5) | 90 | 90 | 90 |
| β, deg | 80.81 (7) | 104.86 (5) | 94.35 (4) | 90 |
| γ, deg | 80.31 (6) | 90 | 90 | 90 |
| *V*, Å$^3$ | 1284 (2) | 4999 (6) | 3015 (3) | 4107 (2) |
| *T*, °C | −120 | −120 | −120 | −120 |
| *Z* | 2 | 4 | 4 | 4 |
| $D_c$, g cm$^{-3}$ | 1.50 | 1.34 | 1.44 | 1.39 |
| μ(Mo Kα), cm$^{-1}$ | 6.5 | 3.7 | 5.7 | 4.8 |
| cryst size, mm | 0.44 × 0.22 × 0.10 | 0.44 × 0.17 × 0.46 | 0.38 × 0.24 × 0.22 | 0.80 × 0.36 × 0.22 |
| cryst color | colorless | colorless | orange | colorless |
| 2θ scan range, deg | 4–45 | 4–45 | 4–50 | 4–50 |
| index ranges | $0 < h < 12$<br>$-12 < k < 12$<br>$-13 < l < 13$ | $0 < h < 12$<br>$0 < k < 30$<br>$-19 < l < 19$ | $0 < h < 12$<br>$0 < k < 22$<br>$-20 < l < 20$ | $0 < h < 24$<br>$0 < k < 24$<br>$0 < l < 13$ |
| no. refl collcd | 3465 | 7003 | 6031 | 4242 |
| no. unique refl | 3355 | 6498 | 5296 | 4058 |
| no. obs refl [$I > 2\sigma(I)$] | 2772 | 3941 | 2565 | 3085 |
| trans, max/min | 0.824/0.755 | 0.781/0.730 | 0.777/0.740 | 0.785/0.704 |
| *R*, $R_w$ | 0.0393, 0.0425 | 0.0599, 0.0577 | 0.104, 0.109 | 0.0523, 0.0533 |
| weighting *g* | 0.00066 | 0.000725 | 0.00090 | 0.00128 |
| Δ/σ max | 0.01 | 0.1 | 0.14 | 0.1 |
| resid peak/hole | 0.36/0.30 | 0.37/0.43 | 0.89/1.16 | 0.35/0.47 |
| data:param ratio | 8.6:1 | 13.7:1 | 7.4:1 | 6.9:1 |

**Table II. Atom Coordinates and Equivalent Isotopic Temperature Factors (Å²)**

| atom | $x$ | $y$ | $z$ | $U_{eq}$ | atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| Compound **2e** | | | | | | | | | |
| Mn(1) | 0.28765 (5) | 0.82150 (5) | 0.60161 (5) | 0.018 | P(1) | 0.3330 (1) | 0.6234 (1) | 0.6956 (1) | 0.017 |
| C(11) | 0.5733 (2) | 0.5162 (2) | 0.6541 (2) | 0.020 | C(12) | 0.6246 (2) | 0.4198 (2) | 0.7409 (2) | 0.026 |
| C(13) | 0.7547 (2) | 0.4068 (2) | 0.7544 (2) | 0.030 | C(14) | 0.8335 (2) | 0.4900 (2) | 0.6812 (2) | 0.033 |
| C(15) | 0.7822 (2) | 0.5864 (2) | 0.5945 (2) | 0.033 | C(16) | 0.6521 (2) | 0.5995 (2) | 0.5809 (2) | 0.024 |
| C(21) | 0.1958 (2) | 0.4323 (2) | 0.7773 (2) | 0.018 | C(22) | 0.0994 (2) | 0.4294 (2) | 0.8743 (2) | 0.022 |
| C(23) | 0.0706 (2) | 0.3134 (2) | 0.9426 (2) | 0.026 | C(24) | 0.1382 (2) | 0.2003 (2) | 0.9139 (2) | 0.027 |
| C(25) | 0.2347 (2) | 0.2032 (2) | 0.8170 (2) | 0.028 | C(26) | 0.2635 (2) | 0.3192 (2) | 0.7486 (2) | 0.022 |
| C(31) | 0.4101 (3) | 0.6824 (3) | 0.8831 (3) | 0.018 | C(32) | 0.3312 (3) | 0.7913 (3) | 0.9072 (3) | 0.017 |
| C(33) | 0.3780 (3) | 0.8626 (3) | 0.9736 (3) | 0.020 | C(34) | 0.4987 (3) | 0.8279 (3) | 1.0107 (3) | 0.024 |
| C(35) | 0.5759 (3) | 0.7193 (3) | 0.9823 (3) | 0.024 | C(36) | 0.5311 (3) | 0.6456 (3) | 0.9198 (3) | 0.020 |
| C(4) | 0.2023 (3) | 0.8326 (3) | 0.8690 (3) | 0.017 | C(5) | 0.1664 (3) | 0.8395 (3) | 0.7619 (3) | 0.018 |
| C(51) | 0.0250 (1) | 0.8837 (2) | 0.7550 (2) | 0.018 | C(52) | –0.0258 (1) | 1.0084 (2) | 0.7642 (2) | 0.023 |
| C(53) | –0.1584 (1) | 1.0469 (2) | 0.7695 (2) | 0.025 | C(54) | –0.2402 (1) | 0.9606 (2) | 0.7656 (2) | 0.024 |
| C(55) | –0.1894 (1) | 0.8359 (2) | 0.7563 (2) | 0.024 | C(56) | –0.0568 (1) | 0.7974 (2) | 0.7511 (2) | 0.020 |
| C(6) | 0.3878 (3) | 0.8076 (3) | 0.4623 (3) | 0.022 | C(7) | 0.4236 (4) | 0.8726 (3) | 0.6504 (3) | 0.022 |
| C(8) | 0.2279 (3) | 0.9912 (4) | 0.5554 (3) | 0.024 | C(9) | 0.1564 (4) | 0.7732 (3) | 0.5393 (3) | 0.022 |
| O(1) | 0.4456 (2) | 0.5250 (2) | 0.6389 (2) | 0.022 | O(2) | 0.2139 (2) | 0.5486 (2) | 0.7074 (2) | 0.018 |
| O(3) | 0.3648 (2) | 0.5971 (2) | 0.8294 (2) | 0.019 | O(6) | 0.4521 (2) | 0.8012 (2) | 0.3730 (2) | 0.029 |
| O(7) | 0.5110 (3) | 0.9107 (3) | 0.6670 (3) | 0.037 | O(8) | 0.1943 (3) | 1.0969 (3) | 0.5323 (3) | 0.039 |
| O(9) | 0.0809 (3) | 0.7443 (3) | 0.4952 (2) | 0.032 | | | | | |
| Compound 3 | | | | | | | | | |
| Mn(1) | 0.5696 (1) | 0.0733 (1) | 0.3820 (1) | 0.025 | P(1) | 0.4235 (2) | 0.0943 (1) | 0.2721 (1) | 0.021 |
| C(4) | 0.5121 (6) | 0.0130 (2) | 0.3981 (4) | 0.028 | C(5) | 0.4680 (6) | 0.1014 (2) | 0.4407 (3) | 0.025 |
| C(6) | 0.6777 (6) | 0.0482 (2) | 0.3241 (4) | 0.031 | C(7) | 0.7005 (6) | 0.0726 (2) | 0.4711 (4) | 0.034 |
| C(11) | 0.5373 (6) | 0.1737 (2) | 0.3118 (3) | 0.023 | C(12) | 0.5546 (6) | 0.2225 (2) | 0.2964 (4) | 0.025 |
| C(13) | 0.6742 (6) | 0.2433 (2) | 0.3337 (4) | 0.029 | C(14) | 0.7676 (6) | 0.2156 (2) | 0.3829 (4) | 0.032 |
| C(15) | 0.7449 (6) | 0.1666 (2) | 0.3964 (4) | 0.027 | C(16) | 0.6278 (6) | 0.1441 (2) | 0.3624 (3) | 0.022 |
| C(21) | 0.2031 (4) | 0.0836 (1) | 0.3091 (2) | 0.022 | C(22) | 0.1936 (4) | 0.0405 (1) | 0.3492 (2) | 0.030 |
| C(23) | 0.1254 (4) | 0.0397 (1) | 0.4070 (2) | 0.034 | C(24) | 0.0668 (4) | 0.0820 (1) | 0.4247 (2) | 0.035 |
| C(25) | 0.0763 (4) | 0.1252 (1) | 0.3846 (2) | 0.027 | C(26) | 0.1444 (4) | 0.1260 (1) | 0.3268 (2) | 0.029 |
| C(27) | 0.1313 (6) | 0.1732 (2) | 0.2740 (4) | 0.032 | C(28) | 0.1233 (6) | 0.1690 (2) | 0.1975 (4) | 0.031 |
| C(31) | 0.3659 (3) | 0.0857 (1) | 0.1149 (2) | 0.019 | C(32) | 0.2663 (3) | 0.0527 (1) | 0.0856 (2) | 0.027 |
| C(33) | 0.1766 (3) | 0.0620 (1) | 0.0140 (2) | 0.025 | C(34) | 0.1865 (3) | 0.1042 (1) | –0.0283 (2) | 0.028 |
| C(35) | 0.2862 (3) | 0.1372 (1) | 0.0009 (2) | 0.023 | C(36) | 0.3759 (3) | 0.1279 (1) | 0.0725 (2) | 0.029 |
| C(37) | 0.2611 (6) | 0.0030 (2) | 0.1281 (4) | 0.029 | C(38) | 0.1457 (6) | –0.0104 (2) | 0.1356 (3) | 0.025 |
| C(39) | 0.4967 (6) | 0.1617 (3) | 0.0955 (4) | 0.032 | C(40) | 0.4732 (6) | 0.2099 (2) | 0.0910 (4) | 0.028 |
| C(211) | 0.1132 (4) | 0.2091 (2) | 0.1404 (2) | 0.035 | C(212) | 0.1650 (4) | 0.2555 (2) | 0.1591 (2) | 0.040 |
| C(213) | 0.1517 (4) | 0.2907 (2) | 0.1002 (2) | 0.056 | C(214) | 0.0866 (4) | 0.2795 (2) | 0.0225 (2) | 0.062 |
| C(215) | 0.0348 (4) | 0.2331 (2) | 0.0039 (2) | 0.060 | C(216) | 0.0482 (4) | 0.1979 (2) | 0.0628 (2) | 0.047 |
| C(221) | 0.1129 (4) | 0.2190 (1) | 0.3150 (2) | 0.029 | C(222) | 0.0033 (4) | 0.2466 (1) | 0.2821 (2) | 0.033 |
| C(223) | –0.0146 (4) | 0.2915 (1) | 0.3152 (2) | 0.045 | C(224) | 0.0771 (4) | 0.3086 (1) | 0.3812 (2) | 0.050 |
| C(225) | 0.1867 (4) | 0.2810 (1) | 0.4142 (2) | 0.053 | C(226) | 0.2046 (4) | 0.2362 (1) | 0.3810 (2) | 0.039 |
| C(311) | 0.1079 (4) | –0.0565 (1) | 0.1666 (2) | 0.029 | C(312) | 0.1560 (4) | –0.1017 (1) | 0.1514 (2) | 0.033 |
| C(313) | 0.1197 (4) | –0.1438 (1) | 0.1846 (2) | 0.035 | C(314) | 0.0354 (4) | –0.1408 (1) | 0.2331 (2) | 0.040 |
| C(315) | –0.0126 (4) | –0.0956 (1) | 0.2483 (2) | 0.036 | C(316) | 0.0236 (4) | –0.0535 (1) | 0.2151 (2) | 0.029 |
| C(321) | 0.3857 (3) | –0.0231 (1) | 0.1538 (2) | 0.023 | C(322) | 0.4731 (3) | –0.0223 (1) | 0.1071 (2) | 0.032 |
| C(323) | 0.5884 (3) | –0.0481 (1) | 0.1305 (2) | 0.047 | C(324) | 0.6164 (3) | –0.0749 (1) | 0.2005 (2) | 0.050 |
| C(325) | 0.5290 (3) | –0.0757 (1) | 0.2471 (2) | 0.044 | C(326) | 0.4136 (3) | –0.0499 (1) | 0.2238 (2) | 0.032 |
| C(331) | 0.6194 (3) | 0.1351 (1) | 0.1117 (2) | 0.022 | C(332) | 0.7150 (3) | 0.1437 (1) | 0.1810 (2) | 0.030 |
| C(333) | 0.8318 (3) | 0.1187 (1) | 0.1953 (2) | 0.038 | C(334) | 0.8530 (3) | 0.0851 (1) | 0.1402 (2) | 0.048 |
| C(335) | 0.7574 (3) | 0.0765 (1) | 0.0709 (2) | 0.044 | C(336) | 0.6406 (3) | 0.1015 (1) | 0.0566 (2) | 0.032 |
| C(341) | 0.5615 (4) | 0.2520 (1) | 0.0948 (2) | 0.028 | C(342) | 0.5022 (4) | 0.2975 (1) | 0.0888 (2) | 0.029 |
| C(343) | 0.5746 (4) | 0.3397 (1) | 0.0886 (2) | 0.037 | C(344) | 0.7063 (4) | 0.3363 (1) | 0.0943 (2) | 0.038 |
| C(345) | 0.7655 (4) | 0.2907 (1) | 0.1003 (2) | 0.042 | C(346) | 0.6932 (4) | 0.2486 (1) | 0.1005 (2) | 0.033 |
| O(1) | 0.4182 (4) | 0.1531 (1) | 0.2705 (2) | 0.022 | O(2) | 0.2735 (4) | 0.0823 (1) | 0.2528 (2) | 0.023 |
| O(3) | 0.4493 (4) | 0.0787 (1) | 0.1905 (2) | 0.021 | O(4) | 0.4788 (4) | –0.0253 (1) | 0.4122 (2) | 0.037 |
| O(5) | 0.4105 (4) | 0.1189 (2) | 0.4796 (3) | 0.038 | O(6) | 0.7457 (4) | 0.0323 (2) | 0.2912 (3) | 0.046 |
| O(7) | 0.7825 (4) | 0.0741 (2) | 0.5283 (3) | 0.048 | | | | | |
| Compound 4 | | | | | | | | | |
| Mn(1) | 0.5105 (2) | 0.1353 (1) | 0.8944 (1) | 0.070 | P(1) | 0.5717 (4) | 0.2268 (2) | 0.9756 (2) | 0.059 |
| O(1) | 0.686 (1) | 0.2213 (5) | 1.0447 (5) | 0.094 | O(2) | 0.455 (1) | 0.2570 (7) | 1.0272 (6) | 0.141 |
| O(3) | 0.6112 (8) | 0.2976 (4) | 0.9319 (4) | 0.042 | C(4) | 0.513 (1) | 0.2055 (6) | 0.7869 (7) | 0.042 |
| C(5) | 0.388 (1) | 0.2173 (8) | 0.8255 (8) | 0.069 | C(6) | 0.319 (2) | 0.151 (1) | 0.8476 (9) | 0.107 |
| O(6) | 0.211 (1) | 0.1263 (8) | 0.8471 (6) | 0.151 | C(7) | 0.473 (2) | 0.0527 (8) | 0.8371 (8) | 0.100 |
| O(7) | 0.450 (1) | –0.0018 (6) | 0.8055 (5) | 0.117 | C(8) | 0.452 (2) | 0.0905 (8) | 0.9832 (9) | 0.098 |
| O(8) | 0.596 (1) | –0.0657 (6) | 0.9636 (5) | 0.116 | C(9) | 0.687 (2) | 0.1089 (8) | 0.8861 (7) | 0.066 |
| O(9) | 0.792 (1) | 0.0884 (5) | 0.8726 (5) | 0.079 | C(11) | 0.791 (1) | 0.1740 (4) | 1.0481 (5) | 0.059 |
| C(12) | 0.780 (1) | 0.1075 (4) | 1.0871 (5) | 0.057 | C(13) | 0.889 (1) | 0.0596 (4) | 1.0924 (5) | 0.095 |
| C(14) | 1.009 (1) | 0.0781 (4) | 1.0587 (5) | 0.120 | C(15) | 1.020 (1) | 0.1446 (4) | 1.0196 (5) | 0.153 |
| C(16) | 0.911 (1) | 0.1926 (4) | 1.0144 (5) | 0.124 | C(21) | 0.469 (1) | 0.3164 (8) | 1.0773 (8) | 0.183 |
| C(22) | 0.491 (1) | 0.3083 (8) | 1.1611 (8) | 0.270 | C(23) | 0.494 (1) | 0.3692 (8) | 1.2113 (8) | 0.368 |
| C(24) | 0.475 (1) | 0.4380 (8) | 1.1776 (8) | 0.303 | C(25) | 0.453 (1) | 0.4461 (8) | 1.0938 (8) | 0.359 |
| C(26) | 0.450 (1) | 0.3852 (8) | 1.0437 (8) | 0.242 | C(31) | 0.6606 (7) | 0.3044 (4) | 0.8568 (3) | 0.037 |
| C(32) | 0.6180 (7) | 0.2657 (4) | 0.7871 (3) | 0.036 | C(33) | 0.6700 (7) | 0.2825 (4) | 0.7133 (3) | 0.046 |
| C(34) | 0.7647 (7) | 0.3381 (4) | 0.7093 (3) | 0.056 | C(35) | 0.8074 (7) | 0.3768 (4) | 0.7790 (3) | 0.063 |

**Table II.** (Continued)

| atom | $x$ | $y$ | $z$ | $U_{eq}$ | atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Compound **4** | | | | | |
| C(36) | 0.7553 (7) | 0.3600 (4) | 0.8528 (3) | 0.056 | C(41) | 0.4956 (7) | 0.1597 (3) | 0.7099 (3) | 0.034 |
| C(42) | 0.3692 (7) | 0.1596 (3) | 0.6665 (3) | 0.030 | C(43) | 0.3488 (7) | 0.1190 (3) | 0.5956 (3) | 0.035 |
| C(44) | 0.4548 (7) | 0.0784 (3) | 0.5679 (3) | 0.034 | C(45) | 0.5812 (7) | 0.0784 (3) | 0.6112 (3) | 0.040 |
| C(46) | 0.6016 (7) | 0.1191 (3) | 0.6822 (3) | 0.034 | C(51) | 0.3262 (9) | 0.2854 (6) | 0.8464 (7) | 0.101 |
| C(52) | 0.2305 (9) | 0.2877 (6) | 0.9040 (7) | 0.151 | C(53) | 0.1561 (9) | 0.3508 (6) | 0.9141 (7) | 0.236 |
| C(54) | 0.1773 (9) | 0.4115 (6) | 0.8665 (7) | 0.217 | C(55) | 0.2730 (9) | 0.4092 (6) | 0.8089 (7) | 0.158 |
| C(56) | 0.3474 (9) | 0.3461 (6) | 0.7988 (7) | 0.104 | | | | | |
| | | | | Compound **6** | | | | | |
| Mn(1) | 0.9832 (1) | 0.1847 (0) | 0.0660 (1) | 0.021 | P(1) | 1.0940 (1) | 0.1802 (1) | 0.0911 (2) | 0.024 |
| P(2) | 0.8742 (1) | 0.1777 (1) | 0.1091 (2) | 0.024 | O(11) | 1.1467 (2) | 0.2105 (2) | −0.0116 (4) | 0.026 |
| O(12) | 1.1192 (2) | 0.1032 (2) | 0.1131 (5) | 0.027 | O(13) | 1.1273 (2) | 0.2158 (2) | 0.2142 (4) | 0.025 |
| O(21) | 0.8174 (2) | 0.2095 (2) | 0.0142 (4) | 0.029 | O(22) | 0.8503 (2) | 0.1008 (2) | 0.1301 (4) | 0.025 |
| O(23) | 0.8444 (2) | 0.2095 (2) | 0.2368 (4) | 0.028 | C(1) | 0.9835 (4) | 0.0940 (3) | 0.0221 (6) | 0.023 |
| C(2) | 0.9820 (4) | 0.2766 (3) | 0.1090 (6) | 0.025 | C(3) | 0.9793 (4) | 0.2128 (3) | −0.1011 (7) | 0.028 |
| O(1) | 0.9846 (3) | 0.0371 (2) | −0.0039 (4) | 0.033 | O(2) | 0.9804 (3) | 0.3345 (2) | 0.1215 (5) | 0.037 |
| O(3) | 0.9782 (3) | 0.2321 (2) | −0.2031 (4) | 0.039 | C(4) | 0.9877 (4) | 0.1476 (3) | 0.2443 (6) | 0.023 |
| C(5) | 0.9903 (4) | 0.1152 (3) | 0.3413 (6) | 0.029 | C(11) | 1.0188 (3) | 0.0075 (2) | 0.4500 (3) | 0.035 |
| C(12) | 1.0228 (3) | −0.0314 (2) | 0.5613 (3) | 0.050 | C(13) | 1.0027 (3) | −0.0040 (2) | 0.6784 (3) | 0.032 |
| C(14) | 0.9786 (3) | 0.0623 (2) | 0.6841 (3) | 0.038 | C(15) | 0.9746 (3) | 0.1012 (2) | 0.5728 (3) | 0.033 |
| C(16) | 0.9947 (3) | 0.0738 (2) | 0.4557 (3) | 0.024 | C(111) | 1.1325 (2) | 0.1383 (2) | −0.1992 (4) | 0.031 |
| C(112) | 1.1376 (2) | 0.1313 (2) | −0.3318 (4) | 0.035 | C(113) | 1.1558 (2) | 0.1868 (2) | −0.4070 (4) | 0.045 |
| C(114) | 1.1687 (2) | 0.2493 (2) | −0.3497 (4) | 0.039 | C(115) | 1.1636 (2) | 0.2563 (2) | −0.2171 (4) | 0.033 |
| C(116) | 1.1454 (2) | 0.2008 (2) | −0.1418 (4) | 0.023 | C(121) | 1.2356 (2) | 0.0713 (3) | 0.0798 (4) | 0.036 |
| C(122) | 1.2977 (2) | 0.0524 (3) | 0.1305 (4) | 0.047 | C(123) | 1.3064 (2) | 0.0487 (3) | 0.2629 (4) | 0.053 |
| C(124) | 1.2530 (2) | 0.0639 (3) | 0.3446 (4) | 0.045 | C(125) | 1.1908 (2) | 0.0827 (3) | 0.2938 (4) | 0.037 |
| C(126) | 1.1822 (2) | 0.0864 (3) | 0.1614 (4) | 0.027 | C(131) | 1.0863 (3) | 0.2991 (2) | 0.3607 (4) | 0.037 |
| C(132) | 1.0792 (3) | 0.3666 (2) | 0.3983 (4) | 0.047 | C(133) | 1.1047 (3) | 0.4184 (2) | 0.3215 (4) | 0.048 |
| C(134) | 1.1373 (3) | 0.4027 (2) | 0.2069 (4) | 0.044 | C(135) | 1.1444 (3) | 0.3353 (2) | 0.1693 (4) | 0.034 |
| C(136) | 1.1189 (3) | 0.2835 (2) | 0.2461 (4) | 0.028 | C(211) | 0.8033 (2) | 0.2586 (2) | −0.1893 (4) | 0.035 |
| C(212) | 0.7962 (2) | 0.2530 (2) | −0.3218 (4) | 0.039 | C(213) | 0.8024 (2) | 0.1900 (2) | −0.3810 (4) | 0.037 |
| C(214) | 0.8157 (2) | 0.1324 (2) | −0.3076 (4) | 0.040 | C(215) | 0.8228 (2) | 0.1380 (2) | −0.1750 (4) | 0.030 |
| C(216) | 0.8166 (2) | 0.2011 (2) | −0.1159 (4) | 0.029 | C(221) | 0.7859 (2) | 0.0771 (2) | 0.3203 (4) | 0.029 |
| C(222) | 0.7253 (2) | 0.0596 (2) | 0.3790 (4) | 0.040 | C(223) | 0.6680 (2) | 0.0489 (2) | 0.3048 (4) | 0.036 |
| C(224) | 0.6712 (2) | 0.0557 (2) | 0.1719 (4) | 0.035 | C(225) | 0.7317 (2) | 0.0733 (2) | 0.1133 (4) | 0.033 |
| C(226) | 0.7891 (2) | 0.0840 (2) | 0.1874 (4) | 0.027 | C(231) | 0.8939 (2) | 0.2863 (2) | 0.3867 (4) | 0.034 |
| C(232) | 0.9030 (2) | 0.3517 (2) | 0.4344 (4) | 0.045 | C(233) | 0.8725 (2) | 0.4067 (2) | 0.3735 (4) | 0.043 |
| C(234) | 0.8330 (2) | 0.3962 (2) | 0.2649 (4) | 0.044 | C(235) | 0.8239 (2) | 0.3308 (2) | 0.2172 (4) | 0.036 |
| C(236) | 0.8544 (2) | 0.2759 (2) | 0.2781 (4) | 0.029 | | | | | |

(s); $^1$H NMR $\delta$ 7.25 (m); $^{13}$C NMR $\delta$ 152.2 (s), 151.7 (s), 132.0 (d), 130.5 (d), 128.6 (d), 126.2 (d), 122.1 (d), 121.9 (d); $^{31}$P NMR $\delta$ 155.8 (s); FAB MS *m/e* 578 [M]$^+$, 550 [M − CO]$^+$, 466 [M − 4CO]$^+$ (base peak), 373 [M − 4CO − OPh]$^+$, 364 [M − 4CO − PhCCH]$^+$.

*Band 4* ($R_f$ = 0.40) was recrystallized from $CH_2Cl_2$/petroleum ether (1:10) to give white crystals of the acetylide complex $PhCCMn(CO)_3[P(OPh)_3]_2$ (**6**) (0.064 g, 3%). Mp: 113–114 °C. Anal. Calcd for $C_{44}H_{35}MnO_6P_2$: C, 65.59; H, 4.10. Found: C, 65.64; H, 4.12. IR: $\nu$(CO) 2057 (s), 1985 (vs), 1965 (s) cm$^{-1}$. $^1$H NMR: $\delta$ 7.23 (m), 7.19 (m). $^{13}$C NMR: $\delta$ 152.5 (s), 131.8 (s), 130.2 (d), 128.4 (d), 125.5 (d), 122.1 (d). $^{13}$P NMR: $\delta$ 163.4. FAB MS: *m/e* 860 [M]$^+$, 776 [M − 3CO]$^+$, 758 [M − PhCCH]$^+$, 683 [M − 3CO − OPh]$^+$, 674 [M − 3CO − PhCCH]$^+$, 590 [M − 3CO − 2OPh]$^+$, 568, 466 [M − 3CO − P(OPh)$_3$]$^+$. The compound was further characterized by X-ray crystallography (see below).

*Band 5* ($R_f$ = 0.25) was an unidentified purple oil (0.004 g) which did not crystallize. This compound does not have any $\nu$(CO) in the 2200–1700-cm$^{-1}$ region. FAB MS: *m/e* 705, 674 (base peak), 633, 619, 488, 364, 327.

*Band 6* ($R_f$ = 0.20) was an unidentified crimson oil (0.039 g) which did not crystallize: IR $\nu$(CO) 2043 (s), 2018 (s), 1967 (s), 1957 (s) cm$^{-1}$; $^{31}$P NMR $\delta$ 128.4; FAB MS *m/e* 938, 882, 836, 759, 710, 675, 490, 400 (base peak), 365.

**X-ray Crystallography.** For compounds **2e**, **3**, **4**, and **6** provisional cell constants and space groups were determined by precession photography. Accurate cell parameters and intensity data were collected using $\omega$-scans on a Nicolet R3 diffractometer with monochromated Mo K$\alpha$ X-rays ($\lambda$ = 0.7107 Å). Empirical absorption corrections were applied, based on $\phi$-scan data. The structures were solved by direct methods and refined using full-matrix least-squares methods, with all non-hydrogen atoms anisotropic. Singly-substituted phenyl rings were treated as rigid hexagons ($d_{C-C}$ 1.39 Å) and for **2e**, **3**, and **6** hydrogen atoms were included in calculated positions with a common temperature factor. Only poor quality crystals were available for the structure determination for **4**, so that the results for this compound are less reliable. The function minimized was $w\Delta F^2$, where $w = [\sigma^2(F) + gF^2]^{-1}$. Crystallographic data are summarized in Table I, atomic coordinates are listed in Table II, and selected bond parameters are given in Table III. The structures showing atom-labeling schemes are in Figures 1–4. All computing was carried out with the SHELX programs.[10]

## Results and Discussion

**Reactions of Orthomanganated Triphenyl Phosphite (1) with Alkynes.** When **1** and $C_2Ph_2$ were irradiated together in benzene, a number of products formed. The major component was identified by spectroscopic methods and by X-ray crystallography[6] as **2a**. Alkyne insertion has occurred into the Mn–C $\sigma$-bond of orthomanganated triphenyl phosphite increasing the metallacyclic ring from five- to seven-membered. The most probable sequence for the alkyne insertion into the Mn–C $\sigma$-bond of orthomanganated triphenyl phosphite (**1**) is CO loss to give a 16-electron species, followed by coordination of the alkyne as an $\eta^2$ ligand, subsequent alkyne insertion into the Mn–C $\sigma$-bond, and base association of CO to give **2a**. In contrast to the postulated corresponding metallacyclic species from the orthomanganated ketones,[1,2] the product **2a** does not undergo

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[10] Sheldrick, G. M. SHELXS86, Program for Solving Crystal Structures. University of Gottingen, 1986; SHELX76, Program for X-ray Crystal Structure Determination. University of Cambridge, 1976.

**Table III. Selected Bond Parameters**

| | | | | | |
|---|---|---|---|---|---|
| | | Bond Lengths (Å) for Compound **2e** | | | |
| Mn(1)---P(1) | 2.212 (1) | Mn(1)---C(5) | 2.114 (4) | P(1)---O(2) | 1.622 (2) |
| P(1)---O(2) | 1.589 (2) | P(1)---O(3) | 1.600 (2) | C(32)---C(4) | 1.474 (5) |
| C(4)---C(5) | 1.342 (5) | C(5)---C(51) | 1.508 (4) | C(11)---O(1) | 1.381 (3) |
| C(31)---O(3) | 1.406 (4) | C(21)---O(2) | 1.377 (3) | C(31)---C(32) | 1.385 (5) |
| | | Bond Angles (deg) for Compound **2e** | | | |
| P(1)–Mn(1)–C(5) | 82.9 (1) | P(1)–Mn(1)–C(6) | 98.0 (1) | P(1)–Mn(1)–C(7) | 92.9 (1) |
| P(1)–Mn(1)–C(8) | 167.1 (1) | P(1)–Mn(1)–C(9) | 89.3 (1) | C(5)–Mn(1)–C(6) | 178.5 (1) |
| C(5)–Mn(1)–C(6) | 178.5 (1) | C(5)–Mn(1)–C(7) | 93.1 (1) | C(5)–Mn(1)–C(8) | 84.2 (1) |
| C(5)–Mn(1)–C(9) | 91.4 (1) | Mn(1)–P(1)–O(1) | 121.2 (1) | Mn(1)–P(1)–O(1) | 121.2 (1) |
| Mn(1)–P(1)–O(1) | 121.2 (1) | Mn(1)–P(1)–O(3) | 119.2 (1) | Mn(1)–C(5)–C(4) | 127.3 (3) |
| Mn(1)–C(5)–C(51) | 117.7 (2) | C(32)–C(4)–C(5) | 128.6 (3) | C(4)–C(5)–C(51) | 114.3 (3) |
| C(32)–C(31)–O(3) | 120.6 (3) | C(36)–C(31)–O(3) | 116.5 (3) | C(31)–C(32)–C(4) | 123.7 (3) |
| O(1)–P(1)–O(2) | 99.4 (1) | O(1)–P(1)–O(3) | 100.8 (1) | O(2)–P(1)–O(3) | 102.5 (1) |
| | | Bond Lengths (Å) for Compound **3** | | | |
| Mn(1)---P(1) | 2.226 (2) | Mn(1)---C(4) | 1.815 (6) | Mn(1)---C(5) | 1.850 (7) |
| Mn(1)---C(6) | 1.859 (7) | Mn(1)---C(7) | 1.814 (6) | Mn(1)---C(16) | 2.097 (6) |
| C(21)---O(2) | 1.389 (6) | C(26)---C(27) | 1.578 (7) | C(27)---C(28) | 1.33 (1) |
| P(1)---O(1) | 1.616 (4) | P(1)---O(2) | 1.593 (4) | P(1)---O(3) | 1.585 (4) |
| C(31)---O(3) | 1.409 (4) | C(32)---C(37) | 1.563 (7) | C(36)---C(39) | 1.562 (7) |
| C(37)---C(38) | 1.33 (1) | C(11)---C(12) | 1.388 (9) | C(39)---C(40) | 1.346 (9) |
| C(11)---O(1) | 1.416 (7) | | | | |
| | | Bond Angles (deg) for Compound **3** | | | |
| P(1)–Mn(1)–C(4) | 100.3 (2) | P(1)–Mn(1)–C(5) | 89.3 (2) | P(1)–Mn(1)–C(6) | 91.4 (2) |
| P(1)–Mn(1)–C(7) | 165.1 (2) | P(1)–Mn(1)–C(16) | 78.0 (2) | Mn(1)–P(1)–O(1) | 106.7 (1) |
| Mn(1)–P(1)–O(2) | 125.4 (2) | Mn(1)–P(1)–O(3) | 117.6 (2) | O(1)–P(1)–O(2) | 100.0 (2) |
| O(1)–P(1)–O(3) | 105.5 (2) | O(2)–P(1)–O(3) | 98.9 (2) | C(12)–C(11)–C(16) | 125.4 (5) |
| C(12)–C(11)–O(1) | 115.7 (5) | C(16)–C(11)–O(1) | 118.8 (5) | Mn(1)–C(16)–C(11) | 117.1 (4) |
| P(1)–O(1)–C(11) | 111.5 (3) | Mn(1)–C(16)–C(15) | 128.1 (4) | P(1)–O(2)–C(21) | 123.4 (3) |
| P(1)–O(3)–C(31) | 126.6 (3) | | | | |
| | | Bond Lengths (Å) for Compound **4** | | | |
| Mn(1)---P(1) | 2.212 (3) | Mn(1)---C(4) | 2.20 (1) | Mn(1)---C(5) | 2.20 (2) |
| Mn(1)---C(6) | 2.01 (2) | C(4)---C(5) | 1.46 (2) | Mn(1)---C(7) | 1.82 (1) |
| Mn(1)---C(8) | 1.82 (1) | C(4)---C(32) | 1.52 (1) | C(5)---C(6) | 1.46 (2) |
| Mn(1)---C(9) | 1.83 (2) | P(1)---O(1) | 1.55 (1) | C(6)---O(6) | 1.16 (1) |
| P(1)---O(2) | 1.59 (1) | P(1)---O(3) | 1.558 (8) | | |
| | | Bond Angles (deg) for Compound **4** | | | |
| P(1)–Mn(1)–C(4) | 91.2 (3) | P(1)–Mn(1)–C(5) | 84.6 (3) | P(1)–Mn(1)–C(6) | 109.4 (5) |
| P(1)–Mn(1)–C(7) | 172.5 (6) | P(1)–Mn(1)–C(8) | 86.9 (4) | C(5)–C(4)–C(32) | 119.7 (9) |
| P(1)–Mn(1)–C(9) | 91.7 (4) | C(32)–C(4)–C(41) | 116.2 (7) | Mn(1)–C(5)–C(4) | 70.6 (8) |
| Mn(1)–C(5)–C(6) | 62 (1) | C(4)–C(5)–C(6) | 114 (1) | C(4)–C(5)–C(51) | 128 (1) |
| Mn(1)–C(6)–O(6) | 141 (2) | C(5)–C(6)–O(6) | 140 (2) | C(7)–Mn(1)–C(8) | 88.6 (5) |
| C(7)–Mn(1)–C(9) | 83.9 (7) | C(8)–Mn(1)–C(9) | 107.7 (8) | Mn(1)–P(1)–O(1) | 123.3 (4) |
| Mn(1)–P(1)–O(2) | 114.6 (3) | O(3)–C(31)–C(32) | 126.4 (4) | Mn(1)–P(1)–O(3) | 115.2 (3) |
| O(1)–P(1)–O(2) | 98.3 (6) | C(4)–C(32)–C(31) | 122.7 (4) | O(1)–P(1)–O(3) | 101.7 (5) |
| O(2)–P(1)–O(3) | 100.0 (6) | P(1)–O(1)–C(11) | 126.0 (7) | P(1)–O(2)–C(21) | 124.2 (7) |
| P(1)–O(3)–C(31) | 127.9 (6) | | | | |
| | | Bond Lengths (Å) for Compound **6** | | | |
| Mn(1)---P(1) | 2.222 (2) | Mn(1)---P(2) | 2.218 (2) | Mn(1)---C(1) | 1.849 (6) |
| Mn(1)---C(2) | 1.868 (6) | Mn(1)---C(3) | 1.833 (7) | Mn(1)---C(4) | 2.002 (6) |
| P(1)---O(11) | 1.613 (5) | P(1)---O(12) | 1.616 (5) | P(1)---O(13) | 1.607 (5) |
| P(2)---O(21) | 1.628 (5) | P(2)---O(22) | 1.605 (4) | P(2)---O(23) | 1.589 (5) |
| C(4)---C(5) | 1.198 (9) | C(5)---C(16) | 1.450 (8) | | |
| | | Bond Angles (deg) for Compound **6** | | | |
| P(1)–Mn(1)–P(2) | 160.6 (1) | P(1)–Mn(1)–C(1) | 89.3 (2) | P(1)–Mn(1)–C(2) | 91.3 (2) |
| P(1)–Mn(1)–C(3) | 99.6 (2) | P(1)–Mn(1)–C(4) | 80.3 (2) | P(2)–Mn(1)–C(1) | 89.6 (2) |
| P(2)–Mn(1)–C(2) | 90.0 (2) | P(2)–Mn(1)–C(3) | 99.8 (2) | P(2)–Mn(1)–C(4) | 80.3 (2) |
| Mn(1)–P(1)–O(11) | 123.4 (2) | Mn(1)–P(1)–O(12) | 111.2 (2) | Mn(1)–P(1)–O(13) | 119.0 (2) |
| Mn(1)–P(2)–O(21) | 122.0 (2) | Mn(1)–P(2)–O(22) | 112.1 (2) | Mn(1)–P(2)–O(23) | 120.7 (2) |
| P(1)–O(11)–C(116) | 126.5 (4) | P(1)–O(12)–C(126) | 123.6 (4) | P(1)–O(13)–C(136) | 124.3 (4) |
| P(2)–O(21)–C(216) | 124.5 (4) | P(2)–O(22)–C(226) | 122.8 (3) | P(2)–O(23)–C(236) | 125.3 (4) |
| Mn(1)–C(4)–C(5) | 169.2 (6) | C(4)–C(5)–C(16) | 177.7 (7) | | |

intramolecular rearrangement so the seven-membered metallacycle can be readily isolated.

The reaction of 1 with $C_2Ph_2$ is most efficient under photolysis, rather than with thermal[1] or with trimethylamine oxide[2] activation which are the most effective methods for orthomanganated ketones. For example, when 1 and $C_2Ph_2$ were refluxed in toluene for 18 h, the major product was again the alkyne-inserted species **2a**, but only in 5% yield. Alternatively, when orthomanganated triphenyl phosphite (**1**) and $Me_3NO$ were dissolved in acetonitrile with $C_2Ph_2$ and stirred for 12 h under nitrogen, a number of compounds were formed but all in very small quantities, so the reaction was not investigated further.

The insertion reaction also occurs between 1 and dimethyl acetylenedicarboxylate under photolysis, to give reasonable yields of the corresponding seven-membered ring complex **2b**.

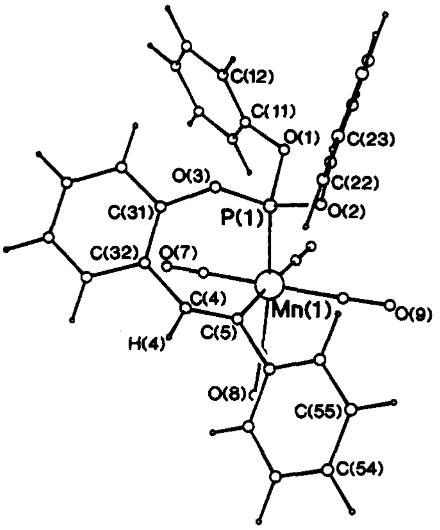

**Figure 1.** Structure of $(PhO)_2\overline{P(OC_6H_4)CH{=}C(Ph)Mn}(CO)_4$ (**2e**).

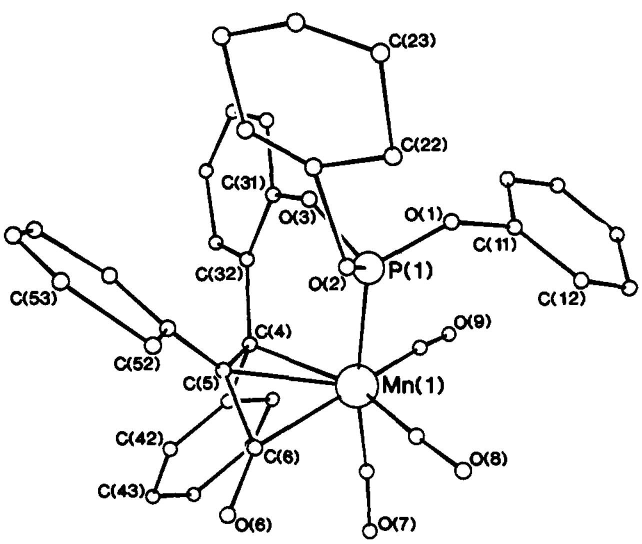

**Figure 2.** Structure of $(PhO)_2\overline{P(OC_6H_4)C(Ph){=}C(Ph)\text{-}C(O)Mn}(CO)_3$ (**4**).

When unsymmetrical alkynes were coupled with orthometalated ketones, only one product isomer was normally found,[1,2] that with the bulkier substituent in the 2-position of the indenol ring after cyclization. Only with acetylenecarboxylate esters did the sterically more crowded alkyne carbon become bonded to the aryl carbon, possibly because of coordination of the ester carbonyl oxygen atom to the manganese.[2] The insertion of the alkyne into the Mn–C bond of orthomanganated ketones is therefore normally regioselective. In contrast, when orthomanganated triphenyl phosphite (**1**) and the unsymmetrical alkyne PhCCH were irradiated in benzene, both possible isomeric insertion products **2e** and **2f** were isolated, with **2e** dominant, as shown unequivocally using X-ray crystallography. The isomers **2e** and **2f** have significantly different carbonyl stretching frequencies and distinctive $^{31}P$ NMR chemical shifts. The unambiguous result for PhCCH, based on the crystal structure, was used as a basis for the spectroscopic characterization of the compounds from the reaction with another unsymmetrical alkyne, $Me_3SiCCH$. For example, the product **2d** has a $^{31}P$ NMR chemical shift and $\nu$(CO) bands similar to those of **2f** and so is assigned with the vinylic hydrogen adjacent to the manganese atom, whereas **2c** has spectroscopic properties similar to those of **2e**, indicating that the bulky substituent, $-SiMe_3$, is adjacent to the manganese atom.

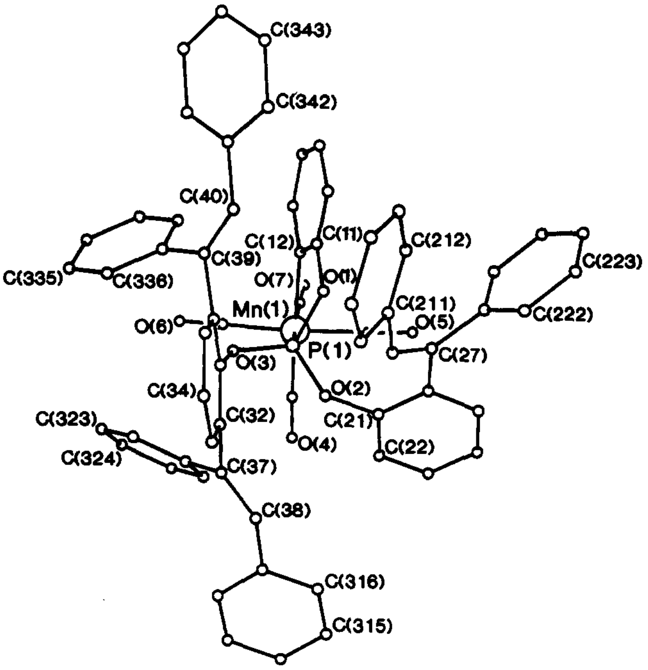

**Figure 3.** Structure of $\{2,6\text{-}[PhCH{=}C(Ph)]_2C_6H_3O\}\{2\text{-}[PhCH{=}C(Ph)]C_6H_4O\}\overline{P(OC_6H_4)Mn}(CO)_4$ (**3**).

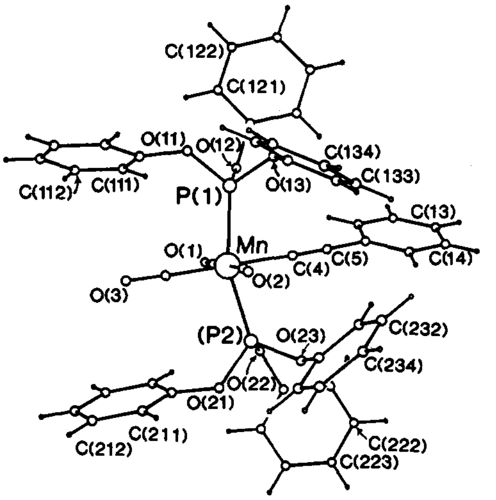

**Figure 4.** Structure of the acetylide complex $PhCCMn(CO)_3[P(OPh)_3]_2$ (**6**).

The regioselectivity of insertion is probably a direct result of preferred orientation for the coordination of the alkyne to the manganese, prior to the insertion step. Theoretical arguments[11] favor a coplanar alignment of the alkyne C≡C bond with the Mn—C $\sigma$-bond. The most favored geometry of the preinsertion intermediate with ketones would be **7**, since the steric interactions will be minimized if the bulkier alkyne substituent is positioned over the CO ligand and not over the aromatic ring. However the results involving orthomanganated triphenyl phosphite with PhCCH or $Me_3SiCCH$ suggest that the alkyne insertion reactions are *not* regioselective. This may be so because the free phenoxy rings interact with the

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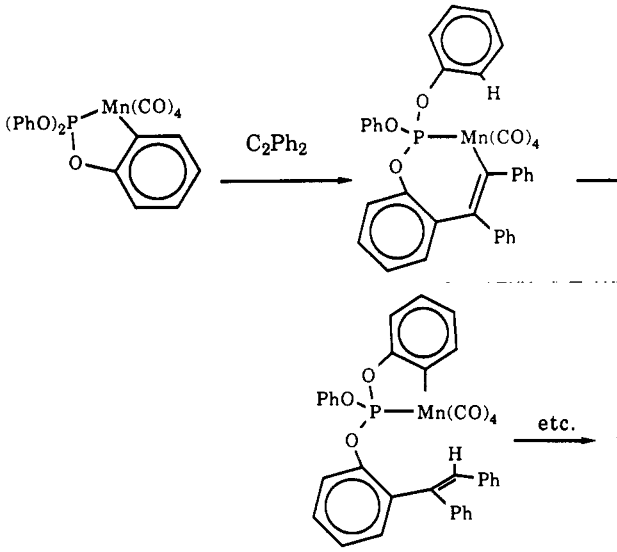
[11] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079.

alkyne substituent so as to reduce the steric preference for one particular orientation. The ratio of isolated products **2e** to **2f** is 1:0.68, with the isomer having the phenyl group adjacent to the manganese atom being dominant. However, for the $Me_3SiCCH$ reaction, equal amounts of the isomers **2c** and **2d** are found.

For all of these results it must be remembered that the reactions of **1** are photochemically induced, in contrast to the thermal reactions with orthomanganated ketones, so it may be that the reaction mechanisms for the two cases are different.

The insertion of an alkyne into the Mn–C bond of **1** to give species **2** generates a new Mn–C bond, into which further insertion of an alkyne is possible, giving nine-membered metallacycles. With $C_2(COOMe)_2$ and **1**, a second product was isolated in 12% yield and tentatively characterized as **5**, arising from a double alkyne insertion. Analytical data and mass spectra show that two alkynes have been added to **1**, while the IR spectrum is characteristic of a cyclometalated tetracarbonylmanganese species and the $^{31}P$ NMR indicates a nine-membered metallacycle, based on the $^{31}P$ chemical shift/ring size correlations discussed below. The most probable structure is therefore **5**, although in the absence of crystallographic data an alternative structure based on one inserted and one ortho 1,2-bis(carboxymethyl)vinyl group (cf. **3** below) cannot be completely excluded. Multiple insertion of alkynes to give large metallacycle rings is rare;[12] a well-characterized example involves the double insertion of $C_2Ph_2$ into the Rh–C bond of $(Ph)_2\overline{P(C_6H_4)Rh}(PPh_3)_2$ to give an eight-membered metallacycle ring,[13] which is however stabilized by coordination of one of the C=C bonds of the ring to the Rh. Multiple insertion to give nine-membered metallacycle rings has been established for some cyclopalladated compounds.[12] It is generally accepted that five-membered metallacycle rings are the most stable, so it is perhaps not surprising that expansion to a nine-membered ring is only observed with $C_2(COOMe)_2$, the most reactive alkyne of those we have used; products analogous to **5** were not detected for any of the other alkynes.

From the reaction of orthomanganated triphenyl phosphite (**1**) with $C_2Ph_2$ a compound was formed which mass spectral and analytical data suggested had incorporated three $C_2Ph_2$ molecules. This was shown crystallographically to be **3**, with three 1,2-diphenylvinyl groups attached to ortho carbon atoms of the nonmetalated phenoxy rings, presumably via alkyne insertion and subsequent intramolecular oxidative addition at the ortho carbon of a second ring which leads to demetalation of the first-formed vinyl group (eq 2).



(2)

Opening of the seven-membered ring by hydrogen-atom transfer and creation of a more stable five-membered one is an interesting extension to alkyne insertion. Repetition of this process would allow multiple alkyne insertions and attachment to phenoxy groups of the triphenyl phosphite ligand. Depending on the alkyne and steric requirements, up to six alkynes could presumably be inserted, of which five would be attached as vinyl groups. The structure **3** is sterically crowded, and it may be that insertion of more $C_2Ph_2$ is inhibited. The reaction is presumably stepwise but isolation of other products from the $C_2Ph_2$ system containing one or two "dangling" alkynes was not achieved, although products of this type may be among the uncharacterized minor components.

There is an obvious parallel here with triphenyl phosphite complexes in which there is specific ortho H/D exchange via a series of orthometalation/demetalation steps,[14] and a related reaction of ethene with ruthenium orthometalated complexes has given ortho-ethylated products, although a similar process was not found in that work for alkynes.[15]

Also isolated from the photochemical reaction of orthomanganated triphenyl phosphite (**1**) with $C_2Ph_2$ was the product **4**, resulting from the insertion of the alkyne and a subsequent insertion of a CO ligand into the new Mn—C $\sigma$-bond. The 16-electron species created by the migratory insertion is stabilized by coordination from the C=C within the metallacyclic ring, so the three-carbon part of the ligand is coordinated in a $\eta^3$-allyl fashion. From the mass spectrum of **4** the base peak is [M - 4CO] which indicates that the CO insertion is reversible, at least within the mass spectrometer. Insertion of what is formally a three-carbon unit [C≡C + CO] into a M—C $\sigma$-bond is not unique, Bruce et al.[16] having reported the insertion of $[C_2(CF_3)_2 + CO]$ into a Co—C $\sigma$-bond to give a corresponding allyl system.

Finally, the last product identified crystallographically was a low-yield species from the reaction of PhCCH with **1**. This proved to be a phenylacetylide complex, $PhC{\equiv}CMn(CO)_3[P(OPh)_3]_2$ (**6**). The route to this is obscure but could involve dissociation of CO from **1**, oxidative addition of the C—H bond of the alkyne to the manganese atom, reductive elimination to generate the C—H arene bond and to liberate the cyclometalated ring, and finally coordination of a phosphite ligand that had been displaced from another manganese atom. Related manganese acetylide complexes have been prepared by a more rational route[17] so this present observation does not represent a useful synthesis.

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[12] Omae, I. *Organometallic Intramolecular Coordination Compounds*; Journal of Organometallic Chemistry Library; Elsevier, Amsterdam, 1986; Vol. 18. Bahsoun, A.; Dehand, J.; Pfeffer, M.; Zinsius, M.; Bouaoud, S. E.; Le Borgne, G. *J. Chem. Soc., Dalton Trans.* **1979**, 547. Maassarani, F.; Pfeffer, M.; Le Borgne, G. *Organometallics* **1987**, *6*, 2029.

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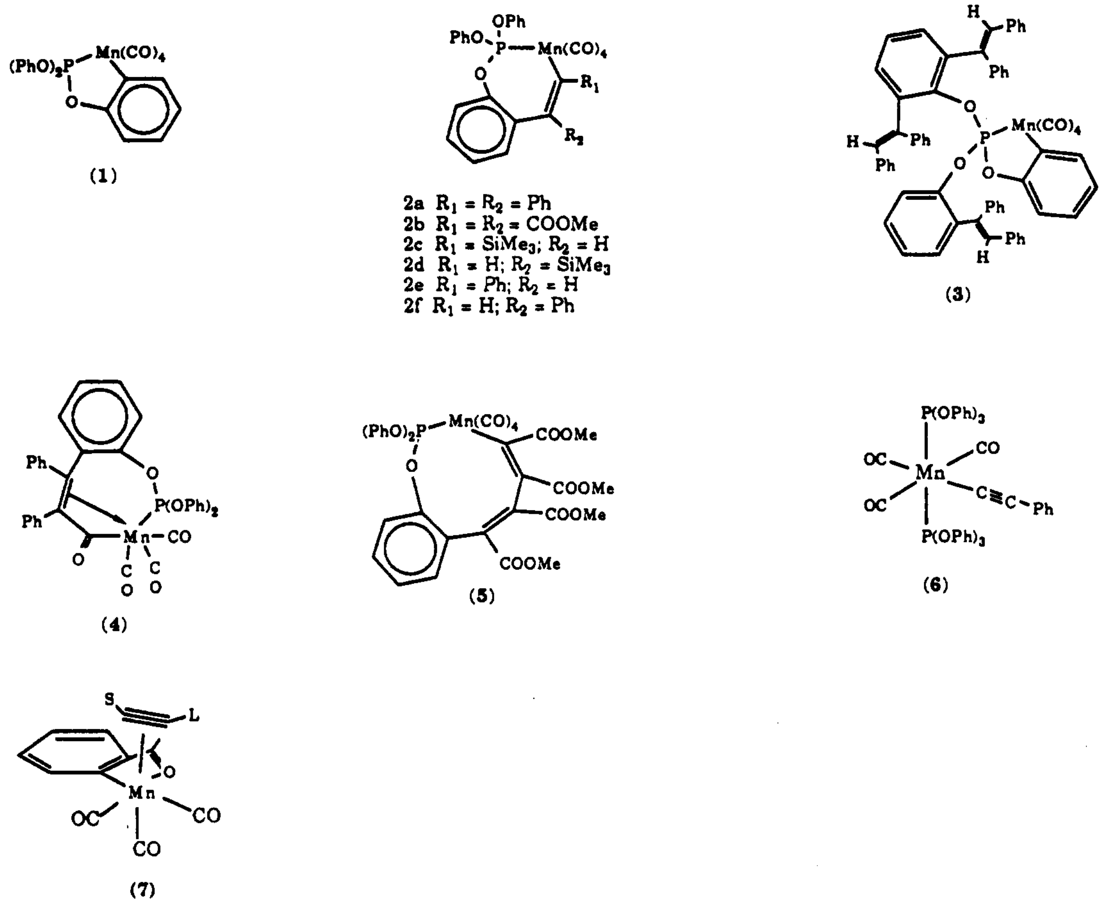
[16] Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1651.

[17] Miguel, D.; Riera, V. *J. Organomet. Chem.* **1985**, *293*, 379.

Chart I



(S = smaller group)
(L = larger group)

A number of other products isolated from the reactions had more than one $P(OPh)_3$ ligand attached to the manganese center. For example metallacyclic compounds related to **2**, but with one CO ligand replaced by $P(OPh)_3$ were invariably found. These were probably formed by intermolecular transfer of $P(OPh)_3$ but since the yields were low it is hard to completely preclude the possibility that they were formed from $P(OPh)_3$-substituted **1**, carried over in small amounts from the initial preparation of the starting material.

**Spectroscopic Data.** For a *cis*-$L_2M(CO)_4$ species four $\nu(CO)$ bands are expected. For some of the compounds studied here only three bands are resolved, with the middle two bands at ca. 2000 $cm^{-1}$ being accidently degenerate. For example, $(PhO)_2\overline{P(OC_6H_4)Mn}(CO)_4$ (**1**) has three bands at 2083 (s), 1998 (vs), and 1971 (s) $cm^{-1}$. However for the alkyne-insertion products **2** four bands are clearly resolved. The separation of the two central bands appears to increase with ring size, being <2 $cm^{-1}$ for five-membered and >15 $cm^{-1}$ for seven-membered rings. Separation is also distinctive for the regioisomers derived from unsymmetrical alkynes. For example, with PhCCH the separation is 18 $cm^{-1}$ for the dominant isomer **2e** in which the Ph group is adjacent to the manganese atom and 14 $cm^{-1}$ for **2f** where the vinylic hydrogen is adjacent to the manganese atom. An additional feature of the IR spectra which distinguishes the two isomers **2e** and **2f** is that each $\nu(CO)$ absorption band for **2e** is 10–15 $cm^{-1}$ higher than the corresponding one observed for **2f**.

Studies[18,19] have clearly established $^{31}P$ NMR as a very sensitive tool for distinguishing a metalated from a nonmetalated phosphine ligand. The $^{31}P$ resonance of the phosphorus ligand commonly moves downfield when the ligand is bonded to a metal atom relative to the free ligand. Shifts can be treated quantitatively by the coordination chemical shift, $\Delta$, defined as $\delta P$(coordination) $- \delta P$(free ligand). Incorporation of phosphorus atoms into a chelate ring makes an additional contribution to the chemical shift, designated $\Delta_R$. Initially these effects were explained on the basis of ring strain. However, examination of four-, five-, and six-membered rings revealed a substantially larger degree of deshielding for the five-membered analogues. There is deshielding of the phosphorus resonance by ~21–33 ppm for chelating phosphorus atoms in five-membered rings, whereas these resonances are shifted to higher field by varying amounts from 2 to 25 ppm for four-, six-, and seven-membered chelate rings. This empirical correlation has been observed in complexes for a large number of metals and geometries and has been reviewed by Garrou.[19]

The $^{31}P$ NMR shifts for some manganese complexes are listed in Table IV; these show a clear relationship between ring size and $^{31}P$ chemical shifts. Orthomanganated triphenyl phosphite (**1**) has a $^{31}P$ chemical shift of 193.0 ppm ($\Delta_R$ = 30.8 ppm), consistent with the deshielding of the phosphorus resonance for a phosphorus atom in a five-membered ring. Alkyne insertion to give a seven-mem-

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(19) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

**Table IV. $^{31}P$ NMR Shifts (δ) for Triphenyl Phosphite Complexes**

| compd | ring size | metalated ligand | free ligand |
|---|---|---|---|
| $P(OPh)_3$ | | | 126.2 |
| $PhCH_2Mn(CO)_4P(OPh)_3$ | | | 159.8 |
| $(PhO)_2P(OC_6H_4)Mn(CO)_4$ (**1**) | 5 | 193.0 | |
| $(PhO)_2P(OC_6H_4)Mn(CO)_3P(OPh)_3$ | 5 | 194.0 | 157.4[a] |
| **3** | 5 | 193.3 | |
| $(PhO)_2P(OC_6H_4)C(R^2){=}C(R^1)Mn(CO)_3L$ | | | |
| L = CO; $R^1 = R^2 = Ph$ (**2a**) | 7 | 171.8 | |
| L = CO; $R^1 = R^2 = COOMe$ (**2b**) | 7 | 172.3 | |
| L = CO; $R^1 = SiMe_3$; $R^2 = H$ (**2c**) | 7 | 176.4 | |
| L = CO; $R^1 = H$; $R^2 = SiMe_3$ (**2d**) | 7 | 156.5 | |
| L = CO; $R^1 = Ph$; $R^2 = H$ (**2e**) | 7 | 166.7 | |
| L = CO; $R^1 = H$; $R^2 = Ph$ (**2f**) | 7 | 155.8 | |
| L = $P(OPh)_3$; $R^1 = R^2 = Ph$ | 7 | 175.2 | 163.8[b] |
| L = $P(OPh)_3$; $R^1 = SiMe_3$; $R^2 = H$ | 7 | 180.3 | 165.0[c] |
| **4** | "8" | 166.4 | |
| **5** | 9 | 146.8 | |

[a] $J_{P-P}$ 102 Hz. [b] $J_{P-P}$ 169 Hz. [c] $J_{P-P}$ 118 Hz.

bered ring results in a $^{31}P$ chemical shift toward higher field, in the range 150–170 ppm ($\Delta_R$ = 5–10 ppm).

The nine-membered ring species **5** has a $^{31}P$ chemical shift of 146.8 ppm, consistent with the empirical relationship.

**X-ray Crystal Structures.** The structure of **2a** has been described elsewhere.[6]

The crystal structure of **2e** was carried out to provide a basis for the assignment of isomers formed by insertion of unsymmetrical alkynes into **1**. The structure is illustrated in Figure 1 and confirms that **2e** is the isomer with the Ph group attached to the carbon atom adjacent to the manganese atom. Other features of the geometry compare closely to those of **2a**. The seven-membered metallacyclic ring of **2e** has adopted a boat conformation, defined by three planes: (i) O3–C(31)–C(32)–C(4) (maximum deviation 0.05 Å), (ii) P(1)–O(3)–C(4)–C(5) (maximum deviation 0.06 Å), and (iii) P(1)–Mn(1)–C(5). The dihedral angle between planes i and ii is 136° (132° for **2a**), while that between planes ii and iii is 138° (135° for **2a**). The dihedral angle between the vinylic phenyl group and that defined by the plane C(4)–C(5)–C(51) is 71°.

The structure of **3** was determined to locate the three $C_2Ph_2$ groups that had been added to **1**. Details are shown in Figure 2. It retains the basic core of **1**, with a five-membered cyclometalated ring involving one of the phenoxy groups of the phosphite ligand. Of the remaining two phenoxy groups, one has a 1,2-diphenylvinyl group substituted at an ortho carbon, while the second has 1,2-diphenylvinyl groups substituted at both ortho carbon atoms.

The five-membered ring can be defined by two planes: (i) P(1)–Mn(1)–O(1) and (ii) Mn(1)–O(1)–C(11)–C(12) (maximum deviation 0.037 Å). The dihedral angle between these planes is 29°, while the dihedral angle between plane ii and the plane defined by the cyclometalated phenyl ring is 4°. In other structures[20] reported for orthomanganated triphenyl phosphite derivatives, the manganese, phosphorus, oxygen, and the six carbon atoms in the orthometalated phenyl group are essentially coplanar. The puckering of the cyclomanganated ring of **3** is clearly due to interactions between the many phenyl groups of the ligand; the molecule is very crowded. However the bond lengths within the orthometalated ring do not significantly differ from those reported[20] for other orthomanganated triphenyl phosphite derivatives.

The structure of **4** is shown in Figure 3. The crystal for this determination was of poor quality leading to a less accurate analysis, so a detailed discussion of bond parameters is not warranted. However the overall features are unambiguous; it is a tricarbonylmanganese derivative with the manganese atom further bonded to the phosphorus atom of the phosphite ligand and to the carbon of an inserted CO ligand. The carbon of the inserted CO is further bonded to a carbon of the alkyne which forms a bridge to the ortho carbon of the phenyl group which was originally bonded to the manganese atom, and the formal double bond C(4)–C(5) is also coordinated to Mn. The insertion of what is formally a three-carbon unit [CO + $C_2Ph_2$] into the Mn–C σ-bond of orthomanganated triphenyl phosphite (**1**) has increased the ring size from five- to eight-membered. The crystal structure of an analogous compound has been reported,[16] resulting from the reaction of a cyclometalated azobenzene cobalt complex with $C_2(CF_3)_2$.

Within the cyclometalated ring of **4**, the Mn(1)–P(1)–O(3)–C(31)–C(32) atoms are essentially coplanar. The dihedral angle between the arene plane and Mn(1)–P(1)–O(3)–C(31)–C(32) is 20° and indicates the cyclometalated phenyl ring is bent with respect to the planar ring. The dihedral angle between the planes O(3)–C(31)–C(32) and C(31)–C(32)–C(4) is 4°, showing only small twisting. The remaining atoms of the cyclometalated ring C(4), C(5), and C(6) adopt a conformation which allows $\eta^3$-allyl coordination to the metal so that the dihedral angle is 60° between the planes C(31)–C(32)–C(4) and C(4)–C(5)–C(6). A similar arrangement was found[16] in the related cobalt complex.

The bond lengths within the cyclometalated ring are typical of an allylic system. The Mn(1)–C(6) bond length is shorter than those of Mn–C(4) and Mn–C(5) but bond lengths C(4)–C(5) and C(5)–C(6) are equivalent.

The structural determination of **6** showed it to be an acetylide complex. Other manganese acetylides that have been structurally characterized include *fac*-$Bu^tCCMn(CO)_3(dppe)$,[21] the CuCl complex of $PhCCMn(CO)_3(dppe)$,[22] and $Ph_3PCCMn(CO)_4Br$, containing a $Ph_3P^+{-}C{\equiv}C^-$ ligand.[23] The manganese in **6** is coordinated to two *trans*-$P(OPh)_3$ ligands and to three CO ligands, with the sixth coordination site occupied by a phenylacetylide ligand. It is therefore the *mer* isomer, in contrast to the two *fac* examples given above with the chelating dppe ligand. The Mn—C(4) bond length of 2.002 (6) Å is that expected for a Mn—C(sp) single bond, and the C(4)—C(5) at 1.198 (9) Å is clearly a triple bond. These values do not differ significantly from the equivalent lengths in *fac*-$Bu^tCCMn(CO)_3(dppe)$, showing little influence from the different ligands trans to the acetylide ligand. The Mn—C(4)—C(5) angle of 169.2° significantly deviates from the expected linearity. Both phosphite groups are bent toward the acetylide, with P—Mn—C(4) angles of 80.3°. A similar, albeit less marked, bending of

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the equatorial ligands toward the acetylide group in *fac*-$Bu^tCCMn(CO)_3(dppe)$ was attributed to the lower steric demands of the acetylide ligand compared with a CO group, resulting from the longer $Mn—C_{acetylide}$ bond compared to the Mn—CO one.

## Conclusions

The photochemical reactions of orthomanganated triphenyl phosphite (1) with alkynes are obviously complex, far more so than the thermal or $Me_3NO$-induced reactions of alkynes with orthomanganated aryl ketones. However, the compounds derived from reactions with 1 indicate the basic processes are (i) insertion of an alkyne into the Mn—C bond to give a seven-membered ring, with a subsequent insertion of a further alkyne into the new Mn—C bond occurring rarely, if at all; (ii) insertion of an alkyne and a CO ligand to give an $\eta^3$-allyl ligand bridging between the arene ring and the metal; (iii) insertion of an alkyne followed by demetalation and orthometalation at a new arene ring to give an *o*-vinyl subsequent on the phenoxy rings; or (iv) for monosubstituted alkynes RCCH formation of a metal acetylide. Under the conditions employed in this study only the first of these occurs in synthetically useful yields, but the other types of products could be favored at different reaction stoichiometries or under CO.

**Acknowledgment.** Financial support from the New Zealand University Grants Committee is gratefully acknowledged. We also thank Dr. Ward T. Robinson and Ms. Jan Wikaira, University of Canterbury, for collection of X-ray intensity data, Professor M. I. Bruce and Dr. C. J. Adams, University of Adelaide, for FABS mass spectra, and Dr. R. Thomson for assistance with NMR spectra.

**Supplementary Material Available:** Tables of anisotropic temperature factors, calculated hydrogen atom positions, and full bond lengths and bond angles for the crystal structures of 2e, 3, 4, and 6 (14 pages). Ordering information is given on any current masthead page.

OM920494B