Reactivity of 1-Alkynes at Dimanganese Carbonyl Centers. Synthesis and Structural Characterization of Alkenyl-, Alkenylidene-, Alkynyl-, and 5-Oxo-2-furanylidene-Bridged Dimanganese Compounds

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Received May 31, 1991

The new unsaturated hydride $[Mn_2(\mu\text{-}H)_2(CO)_6(\mu\text{-dppm})]$ (1) is prepared by treatment of $[Mn_2(\mu\text{-}Cl)_2(CO)_6(\mu\text{-dppm})]$ with 4 equiv of $Li[HBEt_3]$ in tetrahydrofuran at room temperature. 1 reacts with 1-alkynes (R = H, Ph, ^tBu, COOMe) at room temperature to give either hydrido–alkenyl complexes $[Mn_2(\mu\text{-}H)(\mu_2,\eta^1,\eta^2\text{-}CR{=}CH_2)(CO)_6(\mu\text{-dppm})]$ (R = H (3a), Ph (3b)) or alkenylidene species $[Mn_2\text{-}(\mu_2,\eta^1,\eta^2\text{-}C{=}CH^tBu)(CO)_6(\mu\text{-dppm})]$ (4c) and $[(CO)_3Mn(\mu\text{-dppm})\{\mu\text{-}C{=}CHC(O)OMe\}Mn(CO)_3]$ (6). The photochemical reaction of $[Mn_2(CO)_8(\mu\text{-dppm})]$ (2) with 1-alkynes (R = H, Ph, ^tBu, CH_3OCH_2) at -20 °C results in the formation of vinylidene $[Mn_2(\mu_2,\eta^1,\eta^2\text{-}C{=}CHR)(CO)_6(\mu\text{-dppm})]$ (R = Ph (4b), ^tBu (4c), CH_3OCH_2 (4d)), hydrido–alkynyl $[Mn_2(\mu\text{-}H)(\mu_2,\eta^1,\eta^2\text{-}C_2R)(CO)_6(\mu\text{-dppm})]$ (R = H (5a), Ph (5b), ^tBu (5c), CH_3OCH_2 (5d), or 5-oxo-2-furanylidene complexes $[(CO)_4Mn(\mu\text{-dppm})\{\mu_2,\eta^1,\eta^4\text{-}C{—}CH{=}C(R)C(O)O\}Mn(CO)_2]$ (R = H (7a), CH_3OCH_2 (7d)) and $[Mn_2(\mu\text{-}CO)\{\mu_2,\eta^1,\eta^1\text{-}C{—}CH{=}C(R)C(O)O\}(CO)_6(\mu\text{-dppm})]$ (R = H (8a), CH_3OCH_2 (8d)). The relative amounts of the above species depend strongly on the nature of the alkyne and the reaction solvent. The 5-oxo-2-furanylidene ligands in 7 bind the dimetal moiety in a novel μ_2,η^1,η^4-fashion acting as a 6-electron donor. The alkenylidene complexes 4b and 4c can also be obtained through UV irradiation of the alkenyl complex 3a in the presence of an excess of 1-alkyne (R = Ph, ^tBu). Unexpectedly, these complexes isomerize spontaneously in solution at room temperature to yield the corresponding hydrido–alkynyls 5b and 5c. The latter regenerate their vinylidene precursors 4b and 4c by treatment with $Li[AlH_4]$ followed by addition of HBF_4 to the resulting mixture. Complexes 3a, 5a–d, and 7 are stereochemically nonrigid in solution. In the case of the alkynyl species 5 the fluxional process appears to be especially fast, as even evidence for incipient coalescence is not observed down to -90 °C. The structures of 4c, 5b, 6, 7d, and 8d have been fully elucidated by X-ray diffraction studies.

1. Introduction

There is a rich and extensive chemistry derived from the reactions of alkynes with transition-metal substrates. These reactions provide the chemist not only with a new and sometimes unique route to a variety of organic products but also with a great variety of organometallic compounds containing new types of ligands.[2] This work concentrates on the organometallic aspects of these reactions. In this sense, it has been shown that 1-alkynes can originate a great variety of coordinated ligands, such as π-alkynes, vinylidenes, alkynyls, vinyls, carbenes, carbynes, carbides, metallacycles, or π-bonded rings and chains.[3] Each type of ligand, in turn, can achieve different coordination modes at the metal center or centers, and finally,

Scheme I. Some Transformations of 1-Alkynes at Metallic Centers
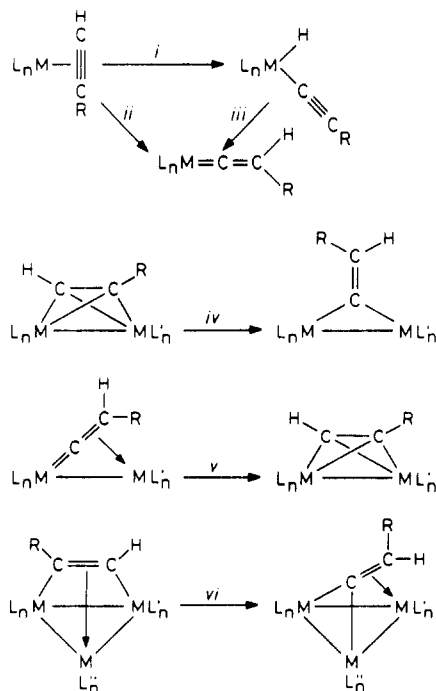
there are several isomerization processes that can transform them into each other. For example, if we consider previously reported π-alkyne, hydrido–alkynyl and vi-

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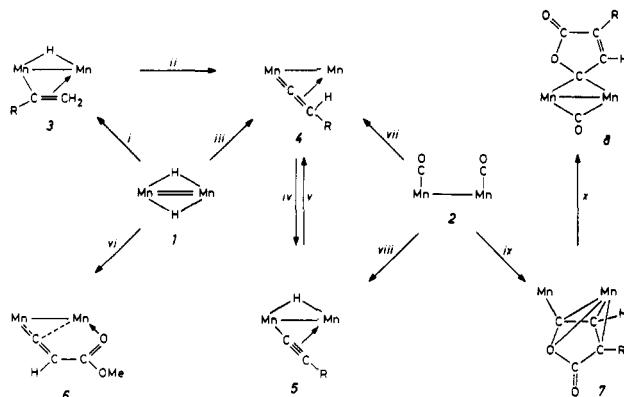
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nylidene compounds, we can find all the transformations shown in Scheme I. Those include η^2-alkyne to hydrido–alkynyl[4] (i) or vinylidene[5] (ii), hydrido–alkynyl to vinylidene[6] (iii), μ_2,η^2,η^2-alkyne to μ_2,η^1,η^1-vinylidene[7] (iv), μ_2,η^1,η^2-vinylidene to μ_2,η^2,η^2-alkyne[8] (v), or $\mu_3,\eta^1,\eta^1,\eta^2$-alkyne to $\mu_3,\eta^1,\eta^2,\eta^1$-vinylidene[9] (vi) isomerizations. In some instances, finally, some of those coordinated ligands can coexist in equilibrium, thus reflecting small differences in their thermodynamic stabilities,[10] which, in turn, means that small changes in the molecule can dramatically affect the nature of the bonded hydrocarbyl ligands under consideration. Not surprisingly, therefore, the factors governing the relative stabilities of those ligands are not yet well understood and the same can be said of the pathways connecting them, although some theoretical work has been done.[11]

In this paper we report the results of our work on the reactivity of the compounds [Mn$_2(\mu$-H)$_2$(CO)$_6(\mu$-L-L)] (1) and [Mn$_2$(CO)$_8(\mu$-L-L)] (2) (L-L = Ph$_2$PCH$_2$PPh$_2$, dppm) toward terminal alkynes. The study of the reactivity of alkynes at dimetallic centers that are bridged by phosphorus ligands has received considerable attention, no doubt because the ligand bridge prevents dimer degradation and also allows for a cooperative activity of the metallic centers.[12,13] Previous work on the reactions of species containing the unsaturated moiety M$_2(\mu$-H)$_2$ (M═M) has been only carried out in detail for [Os$_3(\mu$-H)$_2$(CO)$_{10}$][14] whereas it remains virtually unexplored for the rest.[15,16]

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Scheme II. Reactions of 1-Alkynes with the Dimanganese Complexes 1 and 2 [Mn$_2$ = (CO)$_3$Mn(μ-dppm)Mn(CO)$_3$, Except for Compounds 7, for Which Mn$_2$ = (CO)$_4$Mn(μ-dppm)Mn(CO)$_2$]

Some work has been done on the reactions of alkynes toward dimetallic group 7 compounds. Thus, while the unsaturated compounds [Re$_2(\mu$-H)$_2$(CO)$_6(\mu$-L-L)] [L-L = dppm or (EtO)$_2$POP(OEt)$_2$] failed to react with C$_2$H$_2$,[17] the related compound [Mn$_2(\mu$-H)$_2$(CO)$_4(\mu$-dppm)$_2$] did react with alkynes, but the products were not characterized.[15] By contrast, the saturated species [Mn$_2(\mu$-H)(μ-PPh$_2$)-(CO)$_8$] has been reported to yield hydrido–vinyl complexes in photochemical reactions with alkynes.[18] Finally, the saturated compounds [Re$_2$(CO)$_8(\mu$-L-L)] (L-L = dppm, dmpm) have been shown to incorporate alkynes in the form of vinyl and alkynyl ligands, also under photochemical conditions.[19]

The results we now present here show that, concerning alkyne chemistry, the dimanganese complexes investigated by us exhibit a behavior quite different from those observed for the above mentioned related species. This includes, as most relevant results, (a) the formation of 4-electron donor bridged vinylidene complexes from 1, 2, or hydrido–alkynyl species; (b) the unprecedented spontaneous isomerization of a bridging vinylidene ligand resulting in a hydrido–alkynyl complex, an observation that would have been hardly anticipated on theoretical grounds;[11] (c) the regioselective cocondensation of an alkyne with two CO molecules to give a coordinated 5-

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oxo-2-furanylidene (hereoafter named simply as fura-nylidene) ligand, $\overline{C-CH=CR-C(O)O}$, which is shown to act as a 2- or 6-electron donor. A short account of part of this work has been previously published.[20]

2. Results

2.1. Synthesis of [Mn₂(μ-H)₂(CO)₆(μ-dppm)] (1).

Addition of 4 equiv of Li[HBEt₃] to a tetrahydrofuran solution of [Mn₂(μ-Cl)₂(CO)₆(μ-dppm)]²¹ followed by H₂O yields deep purple [Mn₂(μ-H)₂(CO)₆(μ-dppm)] (1) in moderate yield. Unexpectedly, when only 2 equiv of boron hydride are used, the species isolated is [Mn₂(μ-H)(μ-Cl)(CO)₆(μ-dppm)], a compound previously reported by us.²² In an attempt to gain more understanding about how the formation of 1 occurs, the above experiments were repeated using Li[DBEt₃] and D₂O. Use of 2 equiv of the Li reagent led to the formation of [Mn₂(μ-D)(μ-Cl)-(CO)₆(μ-dppm)], whereas the use of 4 equiv led to [Mn₂-(μ-H)(μ-D)(CO)₆(μ-dppm)]. The characterization of these deuterated species was made by comparison of their ν_{CO} and ¹H and ³¹P NMR data with those corresponding to the nondeuterated species. All attempts to obtain the di-deuterated compound [Mn₂(μ-D)₂(CO)₆(μ-dppm)] were unsuccesful.

2.2. Reactions of [Mn₂(μ-H)₂(CO)₆(μ-dppm)] (1) with 1-Alkynes.

These reactions have been found to yield products whose natures are strongly dependent on the particular alkyne used. Thus acetylene or phenylacetylene lead to vinyl complexes whereas *tert*-butylacetylene yields vinylidene and alkynyl complexes.

(a) Reactions with C₂H₂ and HC₂Ph. Compound 1 smoothly reacts with acetylene or phenylacetylene in tetrahydrofuran at room temperature to give the com-pounds [Mn₂(μ-H)(μ₂,η¹,η²-CR=CH₂)(CO)₆(μ-dppm)] (**3a** for R = H; **3b** for R = Ph) in high yields (i in Scheme II). It should be pointed out that completely pure samples of **3b** could hardly be obtained because of the low thermal stability of this compound in solution; actually, small amounts of the compounds [Mn₂(μ-H)(μ₂,η¹,η²-C₂Ph)-(CO)₆(μ-dppm)] (**5b**) and *fac*-[Mn(CO)₃(C₂Ph)(dppm)]²³ have been identified spectroscopically in the solutions of the vinyl complex **3b**. The spectroscopic data for the vinyl complexes **3a** and **3b** (Table I) are similar and fully con-sistent with the proposed structure. In the case of [Mn₂(μ-H)(μ,η¹,η²-CH=CH₂)(CO)₆(μ-dppm)] (**3a**), the ³¹P{¹H} NMR spectrum at room temperature consists of a single peak at 61.9 ppm, which transforms into an AB system at –50 °C. These facts are indicative of the ex-istence of a fluxional process for **3a** which at room tem-perature effectively equalizes the environments of both metallic centers on the NMR time scale. For compound **3b**, however, there is no evidence of fluxionality at room temperature. In this case, the identification of the vinyl group as μ-CPh=CH₂ rather than μ-CH=CH(Ph) is de-rived from the NMR data. Thus, the ¹H NMR spectrum exhibits two uncoupled resonances at 4.4 and 3.1 ppm for the vinylic protons, and the ¹³C{¹H} NMR spectrum de-notes the presence of two different CH₂ groups, the one at 82.0 ppm being assigned to the β-carbon of the vinyl ligand.

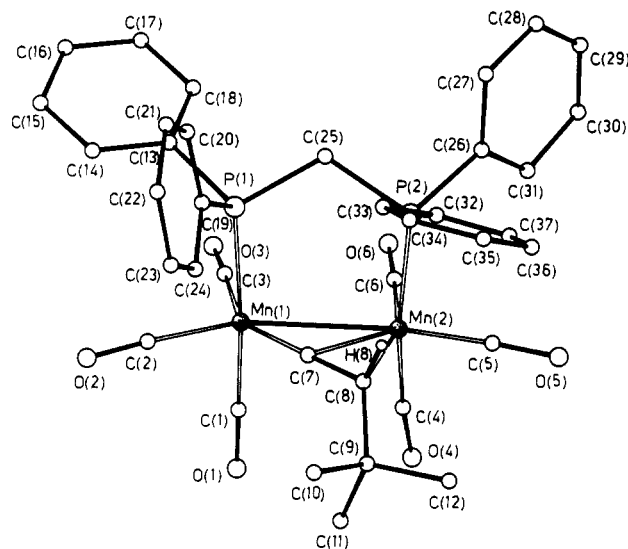(20) García Alonso, F. J.; García Sanz, M.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1167.

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Figure 1. Molecular structure of [Mn₂(μ₂,η¹,η²-C=CHᵗBu)-(CO)₆(μ-dppm)] (**4c**) with the atom-numbering scheme.

(b) Reaction with HC₂ᵗBu. The reaction of 1 with *tert*-butylacetylene at room temperature gives a mixture of the vinylidene and alkynyl complexes [Mn₂(μ₂,η¹,η²-C=CHᵗBu)(CO)₆(μ-dppm)] (**4c**) and [Mn₂(μ-H)(μ₂,η¹,η²-C₂ᵗBu)(CO)₆(μ-dppm)] (**5c**). Monitoring of the reaction by IR and NMR spectroscopy did not show the presence of organometallic species different from **4c** and **5c** at any stage of the reaction. Moreover, those experiments showed that **4c** is the compound initially formed (iii in Scheme II) along with H₂C=CHᵗBu, and that the alkynyl complex **5c** is later formed at the expense of **4c**. The latter process (iv in Scheme II) has been confirmed by separate exper-iments. Thus, a toluene solution of pure **4c** reverts into a solution of pure **5c** if allowed to stand at room tem-perature in the dark for about 1 week. It has also been found that the isomerization **4c** to **5c** is accelerated when the mixture is chromatographed on alumina at room tem-perature.

The structure of the alkenylidene complex **4c** has been confirmed by an X-ray diffraction study, and the molecular structure is depicted in Figure 1. The spectroscopic data (Table I) are consistent with the solid-state structure, the most relevant datum being a strongly deshielded ¹³C{¹H} resonance at 389.5 ppm, indicative of the α-carbon of a σ,π-coordinated vinylidene group.⁸ᵃ The NMR spectra of **4c** are roughly temperature independent, suggesting that the molecule is rigid in solution. An exception to this is found if the ³¹P{¹H} NMR spectra are recorded using CDCl₃ as solvent. Thus while the room-temperature ³¹P{¹H} NMR spectrum of **4c** exhibits the expected AB pattern for the two nonequivalent phosphorus atoms in the molecule, this becomes a singlet below –30 °C. Although we have no explanation for this observation, it seems to be a solvent effect rather than due to a structural change in the mol-ecule, as we have failed to observe this phenomenon when other solvents are used.
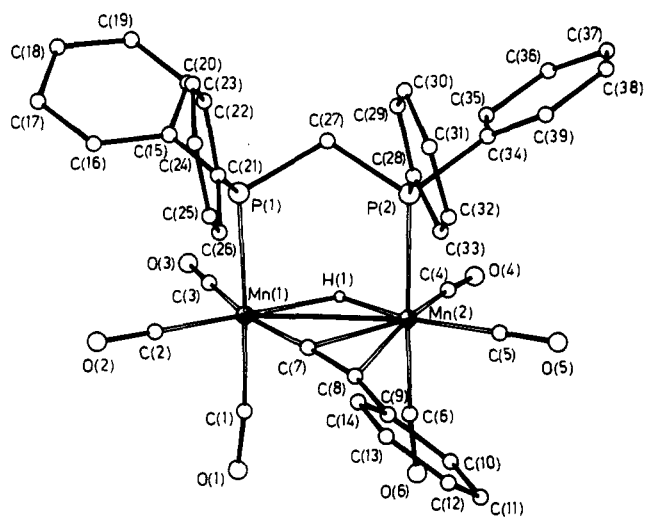
The spectroscopic data for compound **5c** (Table I) evidence the presence of six carbonyls as well as bridging hydride, diphosphine, and alkynyl ligands. The data are also indicative of a symmetrical disposition of those bridging ligands, as it is the case of the related compounds **5a**, **5b**, and **5d** (see later). The proposed structure, how-ever, is based on that determined by X-ray diffraction of [Mn₂(μ-H)(μ₂,η¹,η²-C₂Ph)(CO)₆(μ-dppm)] (**5b**) (Figure 2), which contains an unsymmetrically bridging acetylide ligand of the σ,π-type. Thus, **5c** (and the related ones)

Figure 2. Molecular structure of [Mn$_2$(μ-H)(μ_2,η^1,η^2-C$_2$Ph)-(CO)$_6$(μ-dppm)] (**5b**) with the atom-numbering scheme.

seems to be highly fluxional in solution, as a single resonance remains in its ^{31}P{^{1}H} NMR spectrum, even at –80 °C.

(c) **Reaction with HC$_2$CH$_2$OCH$_3$.** The reaction of compound 1 with an excess of methyl propargyl ether in thf at room temperature gives a complex mixture of products from which no pure compounds could be isolated. The reaction was also carried out using C$_6$D$_6$ as solvent and monitored by NMR spectroscopy. In the latter case, the ^{31}P{^{1}H} NMR spectrum denoted the presence of the vinylidene complex [Mn$_2${μ-C=CH(CH$_2$OMe)}(CO)$_6$(μ-dppm)] (**4d**) (see later) along with other uncharacterized species, one of them supposed to be the vinyl complex [Mn$_2$(μ-H){μ,η^1,η^2-C(CH$_2$OCH$_3$)=CH$_2$}(CO)$_6$(μ-dppm)] because of the similarity of its ^{31}P resonances (AB system, δ_A = 65.0, δ_B = 61.3 ppm and J_{AB} = 109 Hz) with those of the vinyl complexes **3a** and **3b**.

(d) **Reaction with HC$_2$C(O)OMe.** Methyl propynoate reacts with compound 1 at room temperature to give the vinylidene complex [(CO)$_3$Mn(μ-dppm){μ-C=CHC(O)-OMe}Mn(CO)$_3$] (**6**) as major product (vi in Scheme II). The structure of this compound could only be completely elucidated after an X-ray diffraction study, and it is depicted in Figure 3. The spectroscopic data for compound **6** (Table I) are consistent with this solid-state structure. Thus, the ^{13}C{^{1}H} NMR spectrum contains resonances at 350.0 and 122.4 ppm, corresponding to the bridging α- and β-carbon atoms of the vinylidene ligand, respectively. The chemical shift of the β-carbon is indicative of absence of coordination of this atom to the metal center, and correspondingly, the chemical shift of the hydrogen atom attached to this carbon atom is expected to fall in the range 6–7 ppm.[8a] Actually, the vinylidene proton is not apparent in the ^{1}H NMR spectrum of compound **6**, certainly because it is obscured by the phenyl resonances (7.7–6.9 ppm).

When the reaction which leads to compound **6** is monitored by NMR spectroscopy, it is found that H$_2$C=CHC(O)OMe, the olefin resulting from hydrogenation of the employed alkyne, is formed. Moreover, an intermediate metal complex can also be detected. This intermediate exhibits ^{31}P resonances at 83.7 (br) and 66.3 ppm (d, J_{PP} = 72 Hz) and ^{1}H resonances at 6.5 (t, J = 9 Hz) and –11.2 (br) ppm. These data are suggestive of this species being a vinyl complex, probably [(CO)$_3$Mn(μ-H)(μ-dppm){μ-CH=CHC(O)OMe}Mn(CO)$_3$], analogous to **3a** or **3b**. Unfortunately, the low relative amount of this inter-
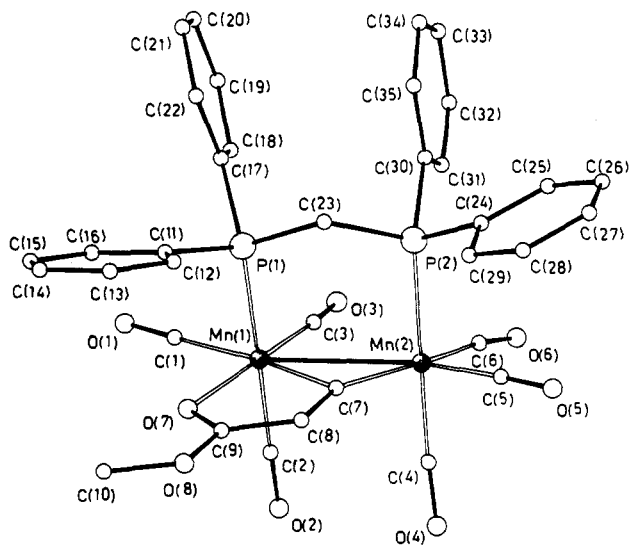
Figure 3. Molecular structure of [(CO)$_3$Mn(μ-dppm)(μ-C=CHC(O)OMe)Mn(CO)$_3$] (**6**) with the atom-numbering scheme.

mediate at any stage of the reaction precluded a more complete characterization.

2.3. Photochemical Reactions of [Mn$_2$(μ-H)(μ_2,η^1,η^2-CH=CH$_2$)(CO)$_6$(μ-dppm)] (3a) with HC$_2$R (R = Ph, ^{t}Bu). Although the vinyl complex [Mn$_2$(μ-H)(μ_2,η^1,η^2-CH=CH$_2$)(CO)$_6$(μ-dppm)] (**3a**) is the only product detected in the reaction of the dihydride complex 1 with an excess of acetylene at room temperature, it was of interest for the present work (see Discussion) to check whether this vinyl complex would be able to react with other 1-alkynes. No reaction takes place when compound **3a** is stirred at room temperature with an excess of HC$_2$R (R = Ph, ^{t}Bu). However, when the mixture is exposed to UV light, the vinylidene complexes **4b** and **4c** are formed respectively in good yield.

2.4. Photochemical Reactions of [Mn$_2$(CO)$_8$(μ-dppm)] (2) with 1-Alkynes. Depending on the particular alkyne used, its photochemical reaction with 2 results in products that either involve carbonyl to alkyne coupling or not. We will describe separately those situations. The first one is found when C$_2$H$_2$ or HC$_2$CH$_2$OCH$_3$ is employed, while no C–C coupling is observed for HC$_2$Ph or HC$_2$^{t}Bu.

(a) **Reactions with C$_2$H$_2$ and HC$_2$CH$_2$OCH$_3$.** UV irradiation of 2 at –20 °C with an excess of HC$_2$R (R = H, CH$_2$OCH$_3$) gives a mixture containing three types of complexes as major species: an alkynyl complex [Mn$_2$(μ-H)(μ_2,η^1,η^2-C$_2$R)(CO)$_6$(μ-dppm)] (R = H (**5a**), CH$_2$OCH$_3$ (**5d**); viii in Scheme II), isostructural with the previously described **5c**, an orange furanylidene compound [(CO)$_4$Mn(μ-dppm){μ_2,η^1,η^4-C—CH=CRC(O)O}Mn(CO)$_2$] (R = H (**7a**), CH$_2$OCH$_3$ (**7d**); ix in Scheme II) in which the heterocyclic bridging ligand acts as an asymmetric 6-electron donor, and a red-violet heptacarbonyl complex [Mn$_2$(μ-CO){μ_2,η^1,η^1-C—CH=CRC(O)O}(CO)$_6$(μ-dppm)] (R = H (**8a**), CH$_2$OCH$_3$ (**8d**); x in Scheme II) which also contains a furanylidene ligand, now providing the metallic centers with only 2 electrons. Other products identified in the reaction mixture are [Mn$_2$(CO)$_6$(μ-dppm)$_2$] and [Mn$_2$(μ-CO)(CO)$_4$(μ-dppm)$_2$],[24] which are the result of partial decomposition of the starting material [Mn$_2$(CO)$_8$(μ-dppm)] under UV irradiation.

We have not found experimental conditions for increasing the selectivity of the above reactions although we

(24) Colton, R.; Commons, C. J. *Aust. J. Chem.* 1975, *28*, 1673.

Table I. Spectroscopic Data for the New Compounds

compd	$\nu_{CO}{}^a$	^{1}H NMR^c	^{13}C{^{1}H} NMR^c	^{31}P{^{1}H} NMR^c
1	2034 (s)	7.4–7.1 (4 *Ph*)		64.4 (s)
	2003 (s)	3.21 (t, J_{PH} = 11, C*H*$_2$)		
	1954 (s)	–17.5 (t, J_{PH} = 21, Mn—*H*—Mn)		
	1921 (s, br)			
3a	2028 (s)^b	7.3 (m, 4 *Ph*)	220.9 (br, 4 *C*O)	61.9 (s)^g
	1990 (s)	6.8 (m, C*H*=CH$_2$)	218.9 (br, 2 *C*O)	
	1955 (m)	5.0 (d, $^3J_{HH}$ = 10, CH=C*H*$_{cis}$H)	164.4 (m, *C*H=CH$_2$)	66.4, 61.8^g
	1930 (s)	4.6 (d, $^3J_{HH}$ = 16, CH=CH*H*$_{trans}$)	137.7–128.5 (4 *Ph*)	(AB system, J_{AB} = 105)
	1918 (s)	3.1 (m), 2.7 (m) (P—C*H*$_2$—P)	83.6 (s, CH=*C*H$_2$)	
	1905 (s)	–17.1 (t, J_{PH} = 19 Mn—*H*—Mn)	29.1 (t, J_{PC} = 12, P—*C*H$_2$—P)	
3b	2030 (s)^b	7.4 (m, 5 *Ph*)	223.0 (br, 2 *C*O)	64.8 (m, 1 *P*)
	1997 (s)	4.4 (s), 3.1 (s), (C*Ph*=CH$_2$)	221.0 (br, 2 *C*O)	63.7 (m, 1 *P*)
	1956 (m)	2.8 (m, P—C*H*$_2$—P)	218.0 (br, 2 *C*O)	
	1933 (m, br)	–17.0 (t, J_{PH} = 25, Mn—*H*—Mn)	155.5 (s, *C*Ph=CH$_2$)	61.7, 59^g
	1903 (m)		135.1–125.3 (5 Ph)	(AB system, J_{AB} = 73)
			82.0 (s, CPh=*C*H$_2$)	
			31.3 (m, P—*C*H$_2$—P)	
4b	2028 (s)	7.9–6.6 (5 *Ph*)		80.1, 78.2
	1974 (s, br)	4.3 (m, C=C*H*Ph)		(AB system, J_{AB} = 121)
	1931 (m)	3.1 (m), 1.9 (m), (C*H*$_2$)		
	1915 (m)			
	1895 (m)			
4c	2025 (s)	8.0–6.5 (4 *Ph*)	389.5 (br, *C*=CH^{t}Bu)^d	79.7, 78.6
	1964 (s, br)	3.5 (m, C=C*H*^{t}Bu)	233.6 (m, *C*O)	(AB system, J_{AB} = 122)
	1917 (m, sh)	3.0 (m), 1.7 (m) (C*H*$_2$)	230.3 (m, 2 *C*O)	
	1910 (m)	1.0 (s, ^{t}*Bu*)	224.9 (m, *C*O)	
	1889 (m)		224.0 (m, *C*O)	
			221.8 (m, *C*O)	
			137.7–129.2 (4 *Ph*)	
			84.7 (s, C=*C*H^{t}Bu)	
			37.2 (s, {*C*(CH$_3$)$_3$})	
			33.2 (m, *C*H$_2$)	
			31.4 (s, {C(*C*H$_3$)$_3$})	
4d	2028 (s)	7.8–6.4 (4 *Ph*)		78.8, 76.7
	1968 (s, br)	4.2 (br, C=C*H*(CH$_2$OCH$_3$)		(AB system, J_{AB} = 121)
	1921 (m, sh)	3.6 (s, CH$_2$OC*H*$_3$)		
	1913 (m)	3.2 (m), 1.9 (m) (P—C*H*$_2$—P)		
	1895 (m)	3.1 (br, C*H*$_2$OCH$_3$)		
5a	2038 (s)	7.3 (br, 4 *Ph*)	222.0 (br, 2 *C*O)	51.0 (s)
	2007 (s)	2.7 (C$_2$*H*)	221.4 (br, 2 *C*O)	
	1959 (m)	2.5 (m), 2.3 (m) (C*H*$_2$)	214.2 (br, 2 *C*O)	
	1940 (m, sh)	–14.3 (t, J_{PH} = 21, Mn—*H*—Mn)	135.6–128.3 (4 *Ph*)	
	1929 (s, br)		74.9 (s, *C*CH)	
			22.2 (t, J_{PC} = 13, *C*H$_2$)	
5b	2036 (s)	7.3 (m, 5 *Ph*)	222.2 (m, 2 *C*O)	52.0 (s)
	2008 (m)	2.6 (m), 2.4 (m) (C*H*$_2$)	221.2 (m, 2 *C*O)	
	1960 (m)	–14.0 (t, J_{PH} = 20, Mn—*H*—Mn)	214.4 (m, 2 *C*O)	
	1940 (m)		135.0–127.2 (5 *Ph*)	
	1928 (s, br)		94.2 (s, C*C*—Ph)	
			24.9 (t, J_{PC} = 13, *C*H$_2$)	
5c	2035 (s)	7.4–7.1 (br, 4 *Ph*)	222.5 (m, 2 *C*O)^e	52.8 (s)^h
	2005 (m)	2.2 (t, J_{PH} = 11, C*H*$_2$)	221.8 (m, 2 *C*O)	
	1956 (m)	1.4 (s, C(C*H*$_3$)$_3$)	214.7 (m, 2 *C*O)	
	1938 (m, sh)	–14.2 (t, J_{PH} = 21, Mn—*H*—Mn)	135.4–128.2 (4 *Ph*)	
	1923 (s, br)		110.3 (t, J_{PC} = 18, *C*—^{t}Bu)	
			107.2 (s, C*C*—^{t}Bu)	
			31.8 (s, {*C*(CH$_3$)$_3$})	
			31.3 (s, {C(*C*H$_3$)$_3$})	
			19.2 (m, *C*H$_2$)	
5d	2037 (s)	7.4–7.1 (4 *Ph*)	222.0 (br, 4 *C*O)	52.5 (s)
	2008 (m)	4.2 (s, C*H*$_2$OCH$_3$)	221.0 (br, 2 *C*O)	
	1957 (m)	3.3 (s, CH$_2$OC*H*$_3$)	136.0–128.3 (4 *Ph*)	
	1939 (m, sh)	2.5 (m), 2.2 (m) (P—C*H*$_2$—P)	88.92 (s, C*C*—CH$_2$OCH$_3$)	
	1928 (s, br)	–14.3 (t, J_{PH} = 20, Mn—*H*—Mn)	64.1 (*C*H$_2$OCH$_3$)	
			57.5 (CH$_2$O*C*H$_3$)	
			21.4 (m, P—*C*H$_2$—P)	
6	2031 (s)	7.7–6.9 (4 *Ph*)	350.0 (m, *C*=CH—C(O)CH$_3$)^d	60.8, 55.1
	1993 (s)	3.1 (m), 2.5 (m) (C*H*$_2$)	228.2, 227.0, 222.2	(AX system, J_{AX} = 101)
	1959 (m)	3.0 (s, C*H*$_3$)	219.9, 218.3, 216.7 (m, 6 *C*O)	
	1941 (m)		181.8 (s, *C*(O)OMe)	
	1917 (m)		137.4–128.0 (4 *Ph*)	
	1868 (w)		122.4 (s, C=*C*H—C(O)OCH$_3$)	
			25.1 (t, J_{PC} = 17, *C*H$_2$)^f	
7a	2083 (m)^b	7.4, 7.2 (m, 4 *Ph*)	231.3 (d, J_{PC} = 23, *C*O)	80.6, 44.9
	1997 (s, br)	5.4 (d, J_{HH} = 3,	223.5 (d, J_{PC} = 13, *C*O)	(AX system, J_{AX} = 43)
	1966 (m, sh)	C—O—C(O)—CH=C*H*)	213.0 (m, 2 *C*O)	

Table I (Continued)

compd	$\nu_{CO}{}^a$	^{1}H NMR^c	^{13}C$\{^1$H$\}$ NMR^c	^{31}P$\{^1$H$\}$ NMR^c
7a	1949 (vs) 1878 (m) 1763 (m, br)	4.2 (d, J_{HH} = 3, C—O—C(O)—C*H*—CH) 3.2 (m, C*H$_2$*)	211.8 (d, J_{PC} = 18, *CO*) 209.8 (d, J_{PC} = 21, *CO*) 160.6 (s, C=O—*C*(O)CH=CH) 137.6–128.0 (4 *Ph*) 103.0 (s, C=O—C(O)—*C*H=CH) 47.6 (s, C—O—C(O)—*C*H=CH) 24.1 (m, *C*H$_2$)	
7d	2083 (m)^b 1998 (s, br) 1967 (m) 1949 (vs) 1878 (s) 1758 (m, br)	7.4–7.1 (4 *Ph*) 5.7 (s, C(CH$_2$OCH$_3$)=C*H*) 4.6, 4.1 (AB system, J_{AB} = 12, C(C*H$_2$*OCH$_3$)=CH) 3.5 (s, C(CH$_2$OC*H$_3$*)=CH) 3.5, 3.3, (m, P—C*H$_2$*—P)	230.9 (d, J_{PC} = 22, *CO*) 223.2 (d, J_{PC} = 14, *CO*) 212.8 (m, 2 *CO*) 211.8 (d, J_{PC} = 20, *CO*) 209.7 (d, J_{PC} = 23, *CO*) 160.0 (s, C—O—*C*(O)-) 136.7–128.0 (4 *Ph*) 105.3 (s, C(CH$_2$OCH$_3$)=*C*H) 66.4 (s, C(*C*H$_2$OCH$_3$)=CH) 62.9 (d, J_{PC} = 3, *C*(CH$_2$OCH$_3$)=CH) 58.2 (s, C(CH$_2$O*C*H$_3$)=CH) 24.1 (m, P—*C*H$_2$—P)	79.4, 45.3 (AX system, J_{AX} = 44)
8a	2042 (m) 2011 (s) 1980 (m) 1956 (m) 1938 (m) 1804 (w) 1726 (m)	8.1 (d, J_{HH} = 4, C(O)—CH=C*H*) 7.5–7.0 (4 *Ph*) 6.1 (d, J_{HH} = 4, C(O)—C*H*=CH) 3.7, 2.0 (m, C*H$_2$*)		56.4 (s)
8d	2042 (m) 2010 (s) 1980 (m) 1956 (m) 1939 (m) 1806 (w) 1722 (m)	8.1 (s, C(CH$_2$OCH$_3$)=C*H*) 7.6–7.0 (4 *Ph*) 4.4 (s, C(C*H$_2$*OCH$_3$)=CH) 3.7, 2.0 (m, P—C*H$_2$*—P) 3.4 (s, C(CH$_2$OC*H$_3$*)=CH)	255.5 (m, μ-*CO*) 219.5 (m, 2 *CO*) 217.9 (m, 2 *CO*) 212.0 (m, 2 *CO*) 186.1 (s, C—O—*C*(O)-) 170.4 (s, C(CH$_2$OCH$_3$)=*C*H) 135.6–128.2 (4 *Ph*) 116.2 (s, *C*(CH$_2$OCH$_3$)=CH) 65.4 (s, C(*C*H$_2$OCH$_3$)=CH) 58.1 (s, C(CH$_2$O*C*H$_3$)=CH) 22.9 (t, J_{PC} = 14, P—*C*H$_2$—P)	56.2 (s)

^{a} In toluene unless otherwise stated; in cm^{-1}. ^{b} In THF. ^{c} In CDCl$_3$, at room temperature, unless otherwise noted. δ in ppm, J in Hz. ^{d} In CD$_2$Cl$_2$ at –60 °C. ^{e} At –60 °C. ^{f} The ^{13}C$\{^1$H$\}$ NMR spectrum in CDCl$_3$ also shows a peak at 52.0 (s) corresponding to the methyl group; this peak is hidden by the methylene chloride signal when CD$_2$Cl$_2$ is used as solvent. ^{g} In CH$_2$Cl$_2$/C$_6$D$_6$ (4:1) at –50 °C. ^{h} In CD$_2$Cl$_2$/CH$_2$Cl$_2$ (1:1) at –80 °C.

have observed that yields of compounds **8a** or **8d** moderately increase if the reactions are carried out under a CO atmosphere. Furthermore, separate experiments indicate that compound **8d** is formed when a solution of pure **7d** is irradiated with UV light while bubbling CO through the solution. However, the overall yield for this reaction is low because **8d** in turn decomposes partially under UV irradiation.

The structures of compounds **7d** and **8d**, containing the furanylidene ligands, have been established by X-ray diffraction studies and are depicted in Figures 4 and 5, respectively. The spectroscopic data for the furanylidene complexes (Table I), suggest that **7a** and **7d** are isostructural as well as **8a** and **8d**. Those data alone, however, would not allow a complete structural characterization of the complexes, although they are in accord with the crystal structures of **7d** and **8d**, thus indicating that the essential features of the solid-state structures are retained in solution. Additionally, compounds **7a** and **7d** display stereochemical nonrigidity in solution, a point which will be later discussed. The spectroscopic data for the above compounds are particularly imprecise in attempting to elucidate the coordination mode of the cyclic furanylidene ligand. Thus, the ^{13}C resonance for the carbene-like carbon atom (C$_\alpha$ in Figure 6) could not be located for any of the compounds investigated. The resonance for C$_\beta$ is located at 170.4 ppm for compound **8d**, which, as expected, shifts upfield upon coordination to a manganese atom, as it occurs in **7d** (105.3 ppm). A similar upfield shift upon metal

coordination is observed for C$_\gamma$ (116.2 and 62.9 ppm for **8d** and **7d**, respectively), and the same applies for the chemical shifts of the protons attached to these carbon atoms. Finally, the resonance for the carbonyl carbon atom C$_\delta$ is also noticeably shifted between **8d** and **7d** (186.1 and 160.0 ppm respectively), even though this carbon atom is never involved in metal bonding. This last fact, therefore, must be interpreted as a consequence of the metal coordination of the vicinal C$_\beta$–C$_\gamma$ bond on going from **8d** to **7d**.

The UV reactions of [Mn$_2$(CO)$_8$(μ-dppm)] (**2**) with 1-alkynes have been found to be sensitive to the nature of the solvent used. Thus, when **2** and HC$_2$CH$_2$OCH$_3$ are irradiated in acetone at –20 °C, the infrared spectrum of the resulting mixture indicates that the major species formed is the vinylidene [Mn$_2$\{μ_2,η^1,η^2-C=CH-(CH$_2$OCH$_3$)\}(CO)$_6$(μ-dppm)] (**4d**) (vii in Scheme II) although small amounts of [Mn$_2$(μ-H)(μ_2,η^1,η^2-C$_2$CH$_2$OCH$_3$)(CO)$_6$(μ-dppm)] (**5d**), [(CO)$_4$Mn(μ-dppm)\{μ_2,η^1,η^4-$\overline{\text{C—CH=C}}$(CH$_2$OCH$_3$)C(O)O\}Mn(CO)$_2$] (**7d**), and [Mn$_2$(μ-CO)\{μ_2-η^1,η^1-$\overline{\text{C—CH=C}}$(CH$_2$OCH$_3$)C-(O)O\}(CO)$_6$(μ-dppm)] (**8d**) are also present, as revealed after column chromatography of the mixture. Surprisingly, when C$_2$H$_2$ is used instead of HC$_2$CH$_2$OCH$_3$, only general decomposition is observed.

Complex **4d** exhibits a low thermal stability. Actually, noticeable decomposition takes place during the purification procedure, which results in the formation of [Mn$_2$(CO)$_6$(μ-dppm)$_2$] and [Mn$_2$(μ-CO)(CO)$_4$(μ-dppm)$_2$],
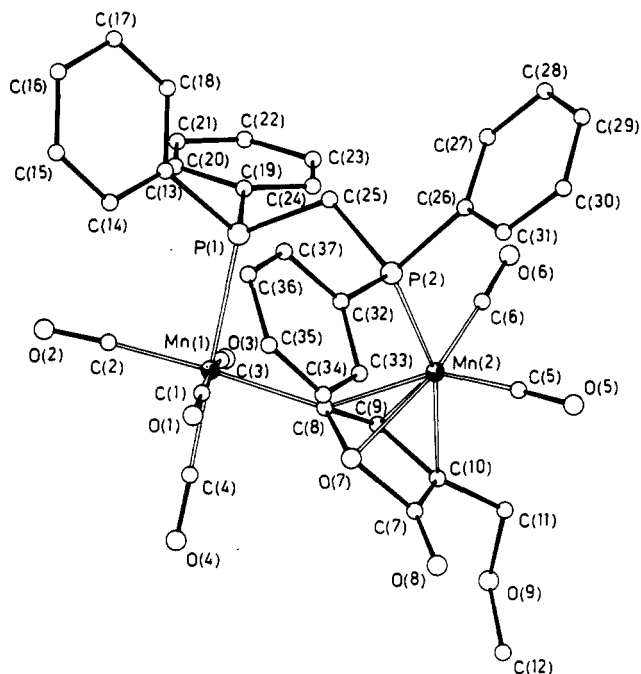
Figure 4. Molecular structure of [(CO)₄Mn(μ-dppm){μ₂,η¹,η⁴-C̅—CH=C(CH₂OCH₃)C(O)O}Mn(CO)₂] (**7d**) with the atom-numbering scheme.
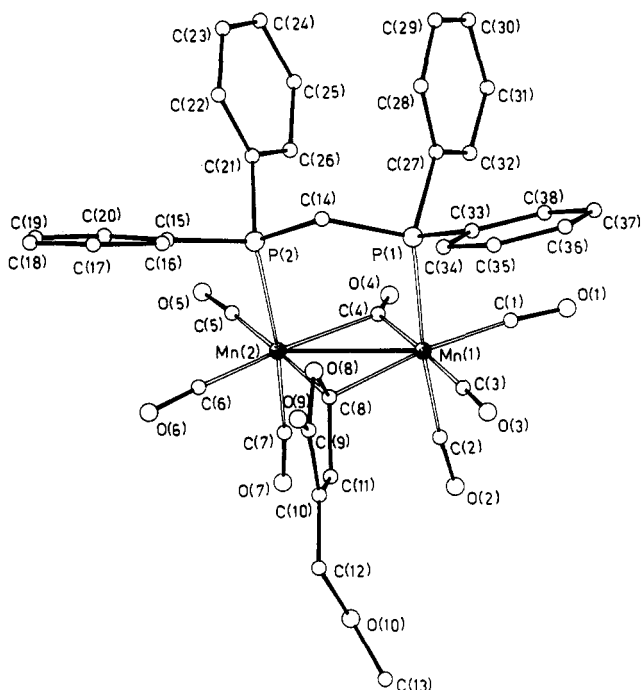
Figure 5. Molecular structure of [Mn₂(μ-CO){μ₂,η¹,η¹-C̅—CH=C(CH₂OCH₃)C(O)O}(CO)₆(μ-dppm)] (**8d**) with the atom-numbering scheme.

thus allowing only small amounts of completely pure **4d** to be isolated. Spectroscopic and microanalytical data for **4d**, however, allow a complete characterization of the complex, which is proposed to be isostructural with the σ,π-vinylidene compound **4c** (Figure 1) on the basis of the close similarity of their IR and ¹H and ³¹P{¹H} NMR spectra.

(b) Reactions with HC₂ᵗBu and HC₂Ph. The UV reaction of [Mn₂(CO)₈(μ-dppm)] (**2**) with HC₂ᵗBu leads to the vinylidene complex [Mn₂(μ₂,η¹,η²-C=CHᵗBu)(CO)₆(μ-

Figure 6. Numbering scheme for furanylidene ligand in compounds **8** (left) and **7** (right) [R = H, CH₂OMe, see text].

dppm)] (**4c**) as main product (vii in Scheme II). As it was the case for the photochemical reactions previously discussed, a strong solvent dependence is also found in this reaction. Thus, **4c** is essentially the only product formed when the reaction is carried out in acetone. However, when toluene is used, significant amounts of the alkynyl complex [Mn₂(μ-H)(μ₂,η¹,η²-C₂ᵗBu)(CO)₆(μ-dppm)] (**5c**) are obtained along with **4c**. Interestingly, when a 30:1 mixture of toluene–tetrahydrofuran is used as solvent, **4c** is again the major product formed, with no **5c** being detected.

An even stronger solvent dependence is found for the photochemical reactions of [Mn₂(CO)₈(μ-dppm)] (**2**) with HC₂Ph. When the reaction is carried out in toluene, the alkynyl complex [Mn₂(μ-H)(μ₂,η¹,η²-C₂Ph)(CO)₆(μ-dppm)] (**5b**) is the major species formed. In acetonitrile, however, the vinylidene complex [Mn₂(μ₂,η¹,η²-C=CHPh)(CO)₆(μ-dppm)] (**4b**) is the major product. In acetone, finally, a mixture of **4b** and **5b** is obtained, which is very difficult to separate.

The structure of the hydrido–alkynyl complex **5b**, determined by an X-ray diffraction study, is depicted in Figure 2. The spectroscopic data in solution (Table I), as it is the case for other complexes reported in this work, cannot be in agreement with the presence of a "static" C₂Ph group bridging the dimetal moiety in an asymmetric σ,π-fashion, thus suggesting that these complexes undergo a fast fluxional process in solution which effectively equalizes the chemical environments around each Mn center.

2.5. Interconversion between Alkenylidene 4 and Hydrido–Alkynyl 5 Compounds. As it has been previously indicated, the vinylidene complex [Mn₂(μ₂,η¹,η²-C=CHᵗBu)(CO)₆(μ-dppm)] (**4c**) isomerizes specifically at room temperature to yield the hydrido–alkynyl complex [Mn₂(μ-H)(μ₂,η¹,η²-C₂ᵗBu)(CO)₆(μ-dppm)] (**5c**). This is also the case of [Mn₂(μ₂,η¹,η²-C=CHPh)(CO)₆(μ-dppm)] (**4b**). However, the other vinylidene compound described in this work, complex **4d**, shows a complicated decomposition process which yields [Mn₂(CO)₆(μ-dppm)₂], [Mn₂(μ-CO)(CO)₄(μ-dppm)₂], and other unidentified species.

We have also found that the reverse transformation, i.e. from **5c** to **4c**, can be accomplished in a two-step reaction (v in Scheme II). Thus, when [Mn₂(μ-H)(μ₂,η¹,η²-C₂ᵗBu)(CO)₆(μ-dppm)] (**5c**) is treated with Li[AlH₄] in thf, gas evolution occurs and a brown solution is formed which, upon acidification with HBF₄, gives a red solution from which [Mn₂(μ₂,η¹,η²-C=CHᵗBu)(CO)₆(μ-dppm)] (**4c**) can be isolated in 62% yield.

A similar procedure gives compound **4b** in 60% yield starting from **5b**. When CF₃CO₂D is used instead of HBF₄, the vinylidene complex [Mn₂(μ₂,η¹,η²-C=CDPh)(CO)₆(μ-dppm)] is formed, which shows IR and NMR spectra identical to those of **4b**, excepting for the resonance at 4.3 ppm, which is now absent in the ¹H NMR spectrum.

The previous two-step reaction fails to yield any vinylidene complex when applied to the alkynyl compound [Mn₂(μ-H)(μ₂,η¹,η²-C₂CH₂OCH₃)(CO)₆(μ-dppm)] (**5d**).

Table II. Important Interatomic Distances (Å) and Angles (deg) for Compounds 4c, 5b, 6, 7d, and 8d

Compound 4c

Mn(1)–Mn(2)	2.800 (5)	Mn(2)–C(4)	1.74 (3)	Mn(1)–C(2)	1.78 (3)	Mn(2)–C(7)	1.95 (2)
Mn(1)–P(1)	2.288 (8)	Mn(2)–C(5)	1.72 (3)	Mn(1)–C(3)	1.81 (3)	Mn(2)–C(8)	2.23 (2)
Mn(1)–C(1)	1.77 (3)	Mn(2)–C(6)	1.77 (3)	Mn(1)–C(7)	1.77 (2)	C(7)–C(8)	1.41 (3)
				Mn(2)–P(2)	2.307 (8)		

P(1)–Mn(1)–Mn(2)	93.5 (2)	C(4)–Mn(2)–Mn(1)	92.8 (9)	C(3)–Mn(1)–Mn(2)	102.9 (9)	Mn(1)–C(7)–C(8)	179 (2)
C(1)–Mn(1)–Mn(2)	90.5 (9)	C(5)–Mn(2)–Mn(1)	170.5 (10)	C(7)–Mn(1)–Mn(2)	43.7 (7)	C(7)–C(8)–C(9)	122 (2)
C(2)–Mn(1)–Mn(2)	153.5 (10)	C(6)–Mn(2)–Mn(1)	83.6 (9)	P(2)–Mn(2)–Mn(1)	94.5 (2)		

Compound 5b

Mn(1)–Mn(2)	2.891 (1)	Mn(2)–C(4)	1.787 (6)	Mn(1)–C(3)	1.802 (7)	Mn(2)–C(8)	2.415 (5)
Mn(1)–P(1)	2.310 (2)	Mn(2)–C(5)	1.798 (7)	Mn(1)–C(7)	1.949 (6)	C(7)–C(8)	1.228 (8)
Mn(1)–C(1)	1.814 (6)	Mn(2)–C(6)	1.812 (7)	Mn(2)–P(2)	2.363 (2)		
Mn(1)–C(2)	1.779 (7)	Mn(2)–C(7)	2.206 (5)				

P(1)–Mn(1)–Mn(2)	92.5 (1)	C(4)–Mn(2)–Mn(1)	108.2 (2)	C(3)–Mn(1)–Mn(2)	115.9 (2)	Mn(1)–C(7)–C(8)	168.0 (5)
C(1)–Mn(1)–Mn(2)	90.5 (2)	C(5)–Mn(2)–Mn(1)	159.1 (2)	C(7)–Mn(1)–Mn(2)	49.7 (2)	C(7)–C(8)–C(9)	161.7 (6)
C(2)–Mn(1)–Mn(2)	147.8 (2)	C(6)–Mn(2)–Mn(1)	90.9 (2)	P(2)–Mn(2)–Mn(1)	91.0 (1)		

Compound 6

Mn(1)–Mn(2)	2.912 (1)	Mn(2)–C(4)	1.796 (4)	Mn(1)–C(3)	1.800 (4)	C(7)–C(8)	1.349 (5)
Mn(1)–P(1)	2.344 (1)	Mn(2)–C(5)	1.786 (4)	Mn(1)–C(7)	2.105 (3)	C(8)–C(9)	1.427 (5)
Mn(1)–C(1)	1.832 (4)	Mn(2)–C(6)	1.832 (5)	Mn(1)–O(7)	2.080 (3)	C(9)–O(7)	1.254 (4)
Mn(1)–C(2)	1.836 (4)	Mn(2)–C(7)	1.865 (4)	Mn(2)–P(2)	2.335 (1)	C(9)–O(8)	1.328 (5)

P(1)–Mn(1)–Mn(2)	92.9 (1)	C(6)–Mn(2)–Mn(1)	114.1 (1)	O(7)–Mn(1)–Mn(2)	117.9 (1)	C(9)–O(7)–Mn(1)	113.5 (2)
C(1)–Mn(1)–Mn(2)	153.9 (1)	C(7)–Mn(2)–Mn(1)	46.1 (1)	C(7)–Mn(1)–O(7)	78.6 (1)	C(7)–C(8)–C(9)	115.6 (3)
C(2)–Mn(1)–Mn(2)	86.8 (1)	Mn(1)–C(7)–Mn(2)	94.2 (2)	P(2)–Mn(2)–Mn(1)	89.3 (1)	C(8)–C(9)–O(7))	120.5 (3)
C(3)–Mn(1)–Mn(2)	66.8 (1)	Mn(1)–C(7)–C(8)	111.7 (3)	C(4)–Mn(2)–Mn(1)	93.3 (1)	C(8)–C(9)–O(8)	118.7 (3)
C(7)–Mn(1)–Mn(2)	39.7 (1)	Mn(2)–C(7)–C(8)	153.2 (3)	C(5)–Mn(2)–Mn(1)	152.2 (2)	O(7)–C(9)–O(8)	120.7 (3)

Compound 7d

Mn(1)–P(1)	2.354 (3)	Mn(2)–C(9)	2.116 (9)	Mn(1)–C(8)	2.060 (8)	C(7)–C(10)	1.407 (13)
Mn(1)–C(1)	1.857 (10)	Mn(2)–C(10)	2.138 (9)	Mn(2)–P(2)	2.213 (3)	C(7)–O(7)	1.459 (11)
Mn(1)–C(2)	1.824 (10)	Mn(2)–O(7)	2.123 (6)	Mn(2)–C(5)	1.780 (11)	C(8)–O(7)	1.467 (10)
Mn(1)–C(3)	1.873 (10)	C(8)–C(9)	1.381 (12)	Mn(2)–C(6)	1.745 (10)	C(7)–O(8)	1.228 (12)
Mn(1)–C(4)	1.801 (10)	C(9)–C(10)	1.413 (13)	Mn(2)–C(8)	2.121 (8)	C(10)–C(11)	1.493 (14)

P(1)–Mn(1)–C(8)	93.8 (2)	O(7)–C(8)–C(9)	103.6 (7)	P(2)–Mn(2)–C(5)	93.3 (3)	C(10)–C(7)–O(7)	105.8 (7)
C(1)–Mn(1)–C(8)	91.1 (4)	C(8)–C(9)–C(10)	113.1 (8)	P(2)–Mn(2)–C(6)	89.7 (3)	C(10)–C(7)–O(8)	136.4 (9)
C(2)–Mn(1)–C(8)	174.7 (4)	C(9)–C(10)–C(7)	106.4 (8)	C(5)–Mn(2)–C(6)	92.3 (5)	O(7)–C(7)–O(8)	117.5 (8)
C(3)–Mn(1)–C(8)	86.0 (4)	C(9)–C(10)–C(11)	128.8 (8)	Mn(1)–C(8)–Mn(2)	141.8 (4)	C(7)–O(7)–C(8)	108.4 (6)
C(4)–Mn(1)–C(8)	85.2 (4)	C(7)–C(10)–C(11)	123.4 (9)				

Compound 8d

Mn(1)–Mn(2)	2.741 (2)	Mn(2)–C(6)	1.768 (9)	Mn(1)–C(4)	1.989 (10)	C(9)–O(9)	1.224 (13)
Mn(1)–P(1)	2.374 (3)	Mn(2)–C(7)	1.809 (13)	Mn(1)–C(8)	2.135 (8)	C(9)–C(10)	1.440 (16)
Mn(1)–C(1)	1.841 (9)	Mn(2)–C(8)	2.037 (9)	Mn(2)–P(2)	2.356 (3)	C(10)–C(11)	1.336 (12)
Mn(1)–C(2)	1.845 (12)	C(8)–O(8)	1.458 (11)	Mn(2)–C(4)	2.189 (9)	C(8)–C(11)	1.461 (12)
Mn(1)–C(3)	1.834 (11)	O(8)–C(9)	1.378 (10)	Mn(2)–C(5)	1.820 (10)	C(10)–C(12)	1.513 (14)

P(1)–Mn(1)–Mn(2)	92.4 (1)	O(8)–C(8)–C(11)	102.2 (7)	C(4)–Mn(2)–Mn(1)	45.9 (3)	C(10)–C(9)–O(8)	107.7 (8)
C(1)–Mn(1)–Mn(2)	139.8 (3)	C(8)–C(11)–C(10)	112.0 (8)	C(5)–Mn(2)–Mn(1)	130.1 (3)	C(8)–O(8)–C(9)	110.2 (6)
C(2)–Mn(1)–Mn(2)	93.3 (3)	C(11)–C(10)–C(12)	131.7 (10)	C(6)–Mn(2)–Mn(1)	133.9 (3)	Mn(1)–C(4)–Mn(2)	81.8 (4)
C(3)–Mn(1)–Mn(2)	126.6 (3)	C(9)–C(10)–C(12)	120.3 (9)	C(7)–Mn(2)–Mn(1)	93.5 (3)	Mn(1)–C(4)–O(4)	144.1 (9)
C(4)–Mn(1)–Mn(2)	52.2 (3)	C(9)–C(10)–C(11)	107.9 (8)	C(8)–Mn(2)–Mn(1)	50.5 (3)	Mn(2)–C(4)–O(4)	132.9 (8)
C(8)–Mn(1)–Mn(2)	47.4 (3)	O(8)–C(9)–O(9)	120.2 (8)	Mn(1)–C(8)–Mn(2)	82.1 (3)		
P(2)–Mn(2)–Mn(1)	93.3 (1)	C(10)–C(9)–O(9)	132.0 (9)				

3. Description of the Structures of 4c, 5b, 6, 7d, and 8d

3.1. [Mn₂(μ₂,η¹,η²-C=CHᵗBu)(CO)₆(μ-dppm)] (4c). A view of the structure of compound 4c is shown in Figure 1 together with the atom-numbering scheme. A summary of the important bond distances and angles is given in Table II. The substitution of two hydrides in 1[20] by the 4-electron donor =C=CHᵗBu ligand, σ,π-interacting, results in the elongation of the unsaturated Mn—Mn bond from 2.699 (2) to 2.800 (5) Å, this latter value being shorter than that found in the structure of Mn₂(CO)₁₀ [2.904 (1) Å],[25] in which a single metal–metal bond must be envi-

saged. The vinylidene group is linearly bonded to the Mn(1) atom, as shown by the Mn(1)–C(7)–C(8) angle, 179 (2)°. The double-bond character of the Mn(1)–C(7) bond is indicated by its length, 1.77 (2) Å, comparable to those involving the terminal carbonyl groups [in the range 1.72 (3)–1.81 (3) Å]. The π interaction between the C(7)–C(8) double bond [1.41 (3) Å] and the Mn(2) atom is rather asymmetrical, the Mn(2)–C(7) and Mn(2)–C(8) lengths being 1.95 (2) and 2.23 (2) Å, respectively. The dppm bridge has an "envelope" conformation with Mn(1), Mn(2), P(1), and P(2) atoms coplanar. The Mn(1), Mn(2), C(7), and C(8) atoms are also strictly coplanar, the two bridges being practically perpendicular to one another [the dihedral angle between them is 91.4 (4)°].

3.2. [Mn₂(μ-H)(μ₂,η¹,η²-C₂Ph)(CO)₆(μ-dppm)] (5b). A view of the structure of compound 5b is shown in Figure 2 together with the atom-numbering scheme. A summary of the important bond distances and angles is given in

(25) Churchill, M. R.; Amoh, K. N.; Wassermann, H. J. *Inorg. Chem.* **1981**, *20*, 1609 (structure determined at room temperature). In the structure determined at low temperature (74 K) the Mn–Mn distance was found 2.895 (1) Å (Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr., Sect. B*, **1982**, *38*, 6).

Table II. In **5b** only one hydride of 1 has been substituted by the 3-electron donor $-C\equiv CPh$ ligand, σ,π-interacting with the $Mn_2(CO)_6(\mu$-dppm) moiety. The Mn–Mn separation is now 2.891 (1) Å, longer than that found in **4c**. The alkynyl group is bound to the Mn(1) atom in a slightly bent way, as shown by the Mn(1)–C(7)–C(8) angle, 168.0 (5)°. The Mn(1)–C(7) bond length is 1.949 (6) Å, slightly shorter than that found for a σ-single bond (see structures of **7d** and **8d**). The π-interaction between the C(7)–C(8) triple bond [1.228 (8) Å] and the Mn(2) atom is again rather asymmetrical, the Mn(2)–C(7) and Mn(2)–C(8) lengths being 2.206 (5) and 2.415 (5) Å, respectively. The hydride bridge [Mn(1)–H(1) = 1.83 (5) and Mn(2)–H(1) = 1.66 (6) Å] is almost coplanar with the alkynyl bridge, whereas the dppm bridge (with Mn(1), Mn(2), P(1), and P(2) atoms coplanar) is almost perpendicular to the other two [dihedral angle 85.2 (1)°].

3.3. [(CO)$_3$Mn(μ-dppm){μ-C=CHC(O)OMe}Mn-(CO)$_3$] (6).

A view of the structure of compound **6** is shown in Figure 3 together with the atom-numbering scheme. A summary of the important bond distances and angles is given in Table II. In **6** the =C=CHC(O)OMe vinylidene ligand, deriving from the starting methyl propynoate, is a 4-electron donor acting either as a bridge between the two Mn atoms through the terminal C(7) atom or as a chelating ligand to the Mn(1) atom through the O(7) atom [Mn(1)–O(7) = 2.080 (3) Å]. The bonding of C(7) to the two metals is asymmetrical, the Mn(1)–C(7) and Mn(2)–C(7) bond distances being 2.105 (3) and 1.864 (4) Å, respectively. The Mn–Mn separation is 2.912 (1) Å, comparable to that found in **5b**. The O(7)–C(9)–C(8)–C(7)–Mn(1) chelate ring is strictly planar with the O(8) and C(10) atoms also lying in the same plane, while the Mn(2) is out by 0.262 (1) Å. The bond distances within the vinylidene ligand are in agreement with an extensive delocalization of the multiple bonds. The dppm bridge (with Mn(1), Mn(2), P(1), and P(2) atoms almost coplanar) is perpendicular to the chelating ring, the dihedral angle being 91.8 (1)°.

3.4. [(CO)$_4$Mn(μ-dppm){μ_2,η^1,η^4-C—CH=C-(CH$_2$OCH$_3$)C(O)O}Mn(CO)$_2$] (7d).

A view of the structure of compound **7d** is shown in Figure 4 together with the atom-numbering scheme. A summary of the important bond distances and angles is given in Table II. The most important feature in the structure of **7d** is the presence of the 5-oxo-2-furanylidene ligand showing an unusual bonding mode and behaving as an asymmetric 6-electron donor to the (OC)$_4$Mn$_2$(CO)$_2$(μ-dppm) moiety. In fact it interacts with Mn(1) though a σ-bond [Mn(1)–C(8) = 2.060 (8) Å] and with Mn(2) through a rather complex bonding system involving four atoms, C(8), C(9), C(10), and O(7), of the pentaatomic ring. The Mn(2)–C(8), Mn(2)–O(7), Mn(2)–C(9), and Mn(2)–C(10) distances, 2.121 (8), 2.123 (6), 2.116 (9), and 2.138 (9) Å, respectively, are very close, while the distance between Mn(2) and the fifth atom of the ring, C(7), is much longer, 2.337 (9) Å. In the furanylidene ligand the pentaatomic ring shows an "envelope" conformation with the four atoms involved in the η^4-interaction with the Mn(2) atom coplanar and the C(7) atom deviating by 0.226 Å from the mean plane passing through them [the Mn(1) and Mn(2) atoms deviate by −0.604 (2) and 1.755 (2) Å, respectively, from the same plane]. Also the C(7)–O(8)–C(10)–O(7) moiety is strictly planar and the two planar fragments are tilted by 12.8 (4)°.

In order to allow both Mn atoms to achieve an 18-electron configuration and an octahedral coordination, the bonding of the furanylidene ligand must be explained with the formation of one σ-bond from C(8) to the Mn(1) atom, one σ-bond from O(7) to Mn(2), and one η^3-interaction from the "allylic" C(8)–C(9)–C(10) system (acting as 3-electron donor) [C(8)–C(9) = 1.381 (12) and C(9)–C(10) = 1.413 (13) Å] to Mn(2). This 6-electron interaction allows for the replacement of two CO ligands and cleavage of the metal–metal bond in the starting compound **2** while the total electron count remains unaltered, an interpretation which is supported by the very long Mn(1)–Mn(2) separation in **7d**, 3.894 (1) Å, clearly a nonbonding length. Moreover, this confirms once again the great flexibility of the dppm bridge, supporting both very short and long metal separations. It is worthy of mention the rather short Mn(2)–P(2) distance, 2.213 (3), if compared with the corresponding Mn(1)–P(1) one, 2.354 (3) Å and with the Mn–P ones found in the other described dppm dimanganese complexes [in the range 2.228 (8)–2.374 (3) Å]. It is difficult to state if steric or electronic effects (or both) are responsible for this short distance.

3.5. [Mn$_2$(μ-CO){μ_2,η^1,η^1-C—CH=C(CH$_2$OCH$_3$)C-(O)O}(CO)$_6$(μ-dppm)] (8d).

A view of the structure of compound **8d** is shown in Figure 5 together with the atom-numbering scheme. A summary of the important bond distances and angles is given in Table II. Compound **8d** has been obtained by substituting in **2** one carbonyl group with the furanylidene ligand interacting as a 2-electron donor ligand and shifting of a carbonyl group from a terminal to a bridging position. The C(8) carbon of the furanylidene ligand is asymmetrically bound through two σ-bonds to the Mn(1) and Mn(2) atoms [Mn(1)–C(8) = 2.135 (8) and Mn(2)–C(8) = 2.037 (9) Å]. This is counterbalanced by the asymmetric carbonyl bridge [Mn(1)–C(4) = 1.989 (10) and Mn(2)–C(4) = 2.189 (9) Å] which is practically coplanar with the C(8) bridge. The dppm bridge (with Mn(1), Mn(2), P(1), and P(2) atoms almost coplanar) is perpendicular to the other two bridges, the dihedral angle being 90.3 (2)°. In spite of the fact that only a single metal–metal bond must be formulated for **8d** to achieve an 18-electron configuration, the Mn–Mn separation, 2.741 (2) Å, is much shorter than those found in **4c**, **5b**, and **6** and close to that found in **1** where a double-bond character of the metal–metal interaction was envisaged. There is currently no clear reason for this shortening of the Mn–Mn distance, although other μ-alkylidene dimetal complexes seem to display this feature.

The pentaatomic ring of the furanylidene ligand is strictly planar (differently from compound **7d**) with also the O(9) and C(12) atoms lying in the same plane and is disposed perpendicularly to the metal–metal bond. The value of the C(10)–C(11) bond, 1.336 (12) Å, is indicative of a localized double bond in the ring.

4. Discussion

4.1. Synthesis of [Mn$_2$(μ-H)$_2$(CO)$_6$(μ-dppm)] (1).

Compound **1** is obtained by treatment of [Mn$_2$(μ-Cl)$_2$-(CO)$_6$(μ-dppm)] with 4 equiv of Li[HBEt$_3$] followed by addition of H$_2$O to the dark green solution thus obtained. The way this reaction proceeds, however, is far from being completely understood nor do we know the nature of the species present in the dark green solution; however, some conclusions can be drawn out from the data given in the Results.

(a) Replacement of each bridging chlorine for a hydrogen atom in the starting material requires 2 equiv of Li[HBEt$_3$], thus excluding a simple substitution of Cl$^-$ by a H$^-$ mechanism.

(b) The substitution of the first chlorine atom to give [Mn$_2$(μ-H)(μ-Cl)(CO)$_6$(μ-dppm)] follows a different path-

Scheme III. Proposed Pathway for the Formation of Alkenylidene Complexes in the Reactions of Compound 1 with 1-Alkynes [Mn₂ = (CO)₃Mn(μ-dppm)Mn(CO)₃]
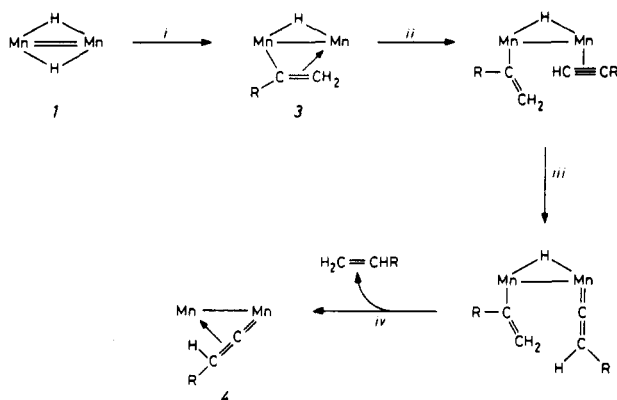
way than the replacement of the second Cl leading to dihydride 1, as it is evidenced by the experiments using Li[DBEt₃] and D₂O, which are summarized in eq 1 ([Mn₂]

$$[Mn_2](\mu\text{-}Cl)_2 \xrightarrow{\text{2Li[DBEt}_3\text{]}} [Mn_2](\mu\text{-}D)(\mu\text{-}Cl) \xrightarrow{\text{2Li[DBEt}_3\text{]}}$$

$$\text{dark green solution} \xrightarrow{\text{D}_2\text{O}} [Mn_2](\mu\text{-}D)(\mu\text{-}H) \quad (1)$$

refers to [Mn₂(CO)₆(μ-dppm)]) Thus the source of the second bridging hydride in 1 is neither the hydride atom of the boron hydride nor the water used in the reaction. A plausible source of this second hydride ligand could be the hydrogen atoms of the ethyl groups present in the boron hydride.

4.2. Reactions of [Mn₂(μ-H)₂(CO)₆(μ-dppm)] (1) with 1-Alkynes. Besides the fact that the nature of the products form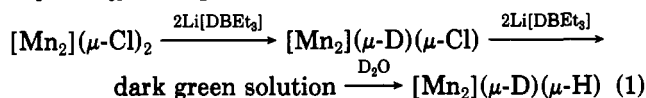ed in the reaction of compound 1 with HC₂R are strongly dependent on R, the results we have obtained suggest that the reaction pathway is very similar in all the cases, the differences arising in the point at which each particular reaction stops. Thus, the initial step would be the alkyne insertion into the Mn–H bond, to give a hydrido–vinyl complex (i in Scheme III). This is also the final point for the cases R = H, Ph. For the other alkynes used in this work, we assume that analogous hydrido–vinyl complexes would be initially formed, which in turn would react with a second alkyne molecule, yielding the vinylidene complex and liberating an alkene molecule. Actually, we have detected intermediate vinyl complexes by NMR monitoring of the reactions of 1 with HC₂CH₂OCH₃ and HC₂C(O)OCH₃ but not for HC₂ᵗBu. In the last case, however, it has been found that the corresponding olefin, H₂C=CHᵗBu, is formed in the reaction, as it is found for the HC₂C(O)OCH₃ reaction, its concentration in the mixture increasing pairwise with that of the vinylidene complex.

Scheme III also contains our proposed pathway connecting the intermediate vinyl complexes with the final vinylidene ones (which is the case for HC₂CH₂OCH₃, HC₂C(O)OCH₃, and HC₂ᵗBu). This could involve three steps, the first being a η² to η¹ slippage of the bridging vinyl ligand, in order to allow coordination of the incoming alkyne (ii in Scheme III). This would be followed by an alkyne to vinylidene isomerization at a single manganese center (iii in Scheme III). This last process has been previously described as happening at several mononuclear metal centers,[5] but it has never been observed at dimetallic centers. By contrast, this process is unknown for manganese compounds; in fact, the complexes [(η⁵-C₅H₅)Mn(CO)₂(η²-HC₂R)] have been reported to be thermally stable[26] and the earlier synthesis of [(η⁵-C₅H₅)Mn(CO)₂(C=

CHR)] from [(η⁵-C₅H₅)Mn(CO)₃] and 1-alkynes[5b] seemed to involve the action of aluminum oxide in the column on the reaction mixture which presumably contained the η²-alkyne species. The final step in our proposed pathway (iv in Scheme III) involves a reductive elimination which produces the observed free alkene and leaves out the σ,-π-vinylidene complex. This type of reductive elimination process has been previously proposed for the reactions of several mono- and trinuclear dihydride complexes with alkynes, which also resulted in the hydrogenation of the alkyne.[27] Further support for the formation of hydrido–vinyl complexes as intermediates in the synthesis of the vinylidene complexes comes from the fact that [Mn₂(μ-H)(μ₂,η¹,η²-CH=CH₂)(CO)₆(μ-dppm)] (3a) reacts under photochemical conditions with HC₂R (R = Ph, ᵗBu) to give the corresponding vinylidene complexes 4b and 4c, respectively. Finally, as the structures of the intermediates proposed after steps ii and iii are concerned, it is interesting to note that they are closely related with the rhenium complex [Re₂(H)(η¹-C₂Ph)(CO)₇(μ-dppm)], the crystal structure of which is known.[19]

Noteworthy, is the stereochemical selectivity in the formation of the vinyl species, as only an isomer of the phenyl–vinyl complex 3b is obtained (the one with the Ph group attached to the α-carbon atom). This is in contrast with the photochemical reactions of saturated dimanganese hydrido compounds with 1-alkynes, which yielded both α- and β-substituted vinyl complexes.[18a] The regioselectivity found in our case could be probably the result of the mild conditions under which the reaction proceeds.

Also noticeable is the different behavior toward 1-alkynes exhibited by compound 1 when compared with related unsaturated dihydrides. Surprisingly, the analogous dirhenium complex [Re₂(μ-H)₂(CO)₆(μ-dppm)] failed to react with 1-alkynes.[17] Although the higher strength of the Re–H bond (as compared with Mn–H) could account for this difference in reactivity, other factors must obviously be involved, as [Os₃(μ-H)₂(CO)₁₀], containing also strong Os–H bonds, does react with 1-alkynes.[14b] Incidentally, β-substituted vinyl groups are formed in the latter case.

4.3. Interconversion between Alkenylidene 4 and Hydrido–Alkynyl 5 Complexes. The vinylidene complexes [Mn₂(μ₂,η¹,η²-C=CHPh)(CO)₆(μ-dppm)] (4b) and [Mn₂(μ₂,η¹,η²-C=CHᵗBu)(CO)₆(μ-dppm)] (4c) spontaneously isomerize in solution at room temperature to give the corresponding hydrido–alkynyl complexes 5b and 5c, no intermediates being detected during this slow transformation. While hydrido–alkynyl to vinylidene isomerizations have been previously reported,[6] to our knowledge there are no previous examples of the reverse isomerization either in mononuclear or binuclear compounds. In fact, theoretical calculations by Silvestre and Hoffmann[11] led to the conclusion that μ₂-hydrido–μ₂,η¹,η¹-alkynyl to μ₂,η¹,η¹-vinylidene isomerization, and not the reverse, would be a feasible process at a dinuclear center. Recently, however, Ewing and Farrugia[10a] have reported the case of a triruthenium–platinum cluster which in solution exists as a mixture of two isomers in equilibrium, the minor one being a hydrido–alkynyl species and the major one a vinylidene complex. However, this ligand isomerization is accompanied by extensive cluster rearrangement, a fact which precludes further conclusions from being drawn out.

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Scheme IV. Alternative Pathways Proposed for the Alkenylidene to Hydrido–Alkynyl Thermal Isomerization [Mn$_2$ = (CO)$_3$Mn(μ-dppm)Mn(CO)$_3$]
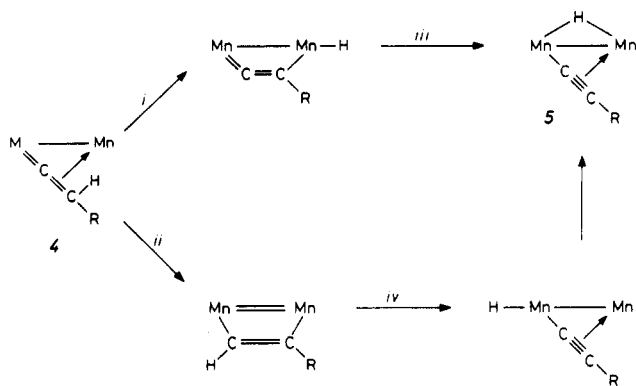
Scheme V. Hydrido–Alkynyl to Alkenylidene Transformations [Mn$_2$ = (CO)$_3$Mn(μ-dppm)Mn(CO)$_3$, R = Ph, ^{t}Bu]^a
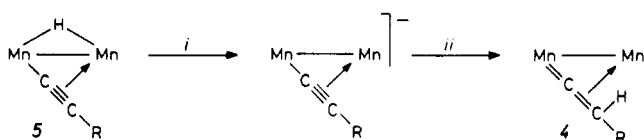

^{a} Legend: (i) Li[AlH$_4$], THF, room temperature; (ii) HBF$_4$, THF, room temperature.

Isomerization of the vinylidene complexes **4b** and **4c** into the corresponding hydrido–alkynyl species **5b** and **5c** requires the hydrogen bonded to the β-carbon of the vinylidene ligand to shift up to the metal atoms. This can be accomplished, in principle, either by direct oxidative addition of the C–H bond (i in Scheme IV) or via H migration through the α-carbon (ii in Scheme IV), giving some sort of alkyne complex and further alkyne to hydrido–alkynyl transformation. While both routes involve reasonable steps, we favor sequence i–iii, taking into account the fact that the vinylidene compound [(CO)$_3$Mn-(μ-dppm){μ-C=CHC(O)OMe}Mn(CO)$_3$] (6) does not isomerize to give a hydrido–alkynyl complex. Thus, because the β-carbon in the vinylidene ligand in 6 is uncoordinated and far away from the metal centers (see Figure 3), it is expected that the corresponding C–H bond could not approach the manganese atom, as required for C–H oxidative addition (step i in Scheme IV), while we see no reason why this would preclude an α,β-hydrogen shift in the vinylidene ligand (step ii in Scheme IV) which could afterwards be followed by coordination of the β-carbon atom.

Although the vinylidene to hydrido–alkynyl isomerization is irreversible for the compounds reported in this work, the reverse process can be accomplished by deprotonation of the hydrido–alkynyl complex and further protonation of the resulting intermediate, presumably an anionic alkynyl complex (Scheme V). A similar deprotonation-protonation process has sucessfully been used in the synthesis of [Mo$_2$(μ_2,η^1,η^2-C=CHPh)(CO)$_4$(η^5-C$_5$H$_5$)$_2$] from the alkyne complexes [Mo$_2$(μ_2,η^2,η^2-HC$_2$Ph)(CO)$_4$(η^5-C$_5$H$_5$)$_2$].[8b]

4.4. Photochemical Reactions of [Mn$_2$(CO)$_8$(μ-dppm)] (2) with 1-Alkynes. Reactions of compound 2 with 1-alkynes HC$_2$R (R = H, Ph, ^{t}Bu, CH$_2$OCH$_3$) are obviously quite complex, considering the structural diversity of the products formed. The reacting alkyne has been found coordinated to the dimetal center in the form of vinylidene, hydrido–alkynyl, μ_2,η^1,η^4-furanylidene, or μ_2,η^1,η^1-furanylidene ligands (compounds 4, 5, 7, or 8, respectively).

Scheme VI. Proposed Pathways Describing the Photochemical Reactions of Compound 2 with 1-Alkynes [Mn$_2$ = (CO)$_3$Mn(μ-dppm)Mn(CO)$_3$, Except for Complexes 7; See Text]
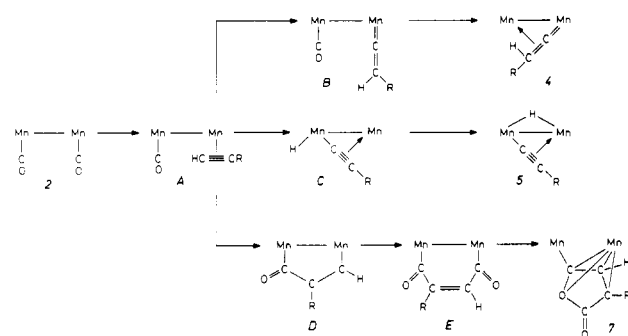
As indicated before, complexes [Mn$_2$(μ-CO){μ_2,η^1,η^1-C—CH=CRC(O)O(CO)$_6$(μ-dppm)] (8) are formed from [(CO)$_4$Mn(μ-dppm){μ_2,η^1,η^4-C—CH=CRC(O)O}Mn(CO)$_2$] (7) under the reaction conditions. This process involves a formal slippage of the furanylidene ligand from a μ_2,η^1,η^4-fashion (6-electron donor), into a μ_2,η^1,η^1-one (2-electron donor), the 4-electron difference being compensated for by the coordination of a CO molecule and the formation of a metal–metal bond. It is interesting to note that the reverse transformation, i.e., 8 to 7 does not occur under UV conditions, which in principle could favor the necessary steps: decarbonylation and metal–metal cleavage. On the other hand, separate experiments indicate that none of the compounds 4, 5, or 7 is formed from any of the others. Finally, the isomerization of [Mn$_2$(μ-C=CHR)-(CO)$_6$(μ-dppm)] (4) to [Mn$_2$(μ-H)(μ_2,η^1,η^2-C$_2$R)(CO)$_6$(μ-dppm)] (5) does not take place at any appreciable extent at -20 °C. Therefore, independent pathways must be responsible for the formation of each of these three types of complexes.

It is reasonable to assume that the UV irradiation would promote the loss of a CO molecule in [Mn$_2$(CO)$_8$(μ-dppm)] (2) as the first step, thus allowing coordination of the incoming alkyne in a η^2-fashion (Scheme VI). The resulting intermediate A could afterwards experience three different and mutually competitive processes: (a) 1,2-hydrogen shift leading finally to the vinylidene complexes 4; (b) C–H oxidative addition giving the hydrido–alkynyl complexes 5; (c) a series of carbonyl to alkyne couplings, affording the furanylidene complexes 7 (and thus also 8).

The 1,2-hydrogen shift pathway is much the same as the one proposed for the formation of the vinylidene complexes from the dihydrido compound 1 and 1-alkynes (see Scheme III) and would yield a η^1-vinylidene heptacarbonyl intermediate B, which under UV action would lose another CO molecule to give the final μ,σ,π-vinylidene complexes 4.

The C–H oxidative addition pathway is the best documented one, as it was found to be the dominant process occurring during the UV reactions of 1-alkynes with [Re$_2$(CO)$_8$(μ-dppm)].[19] In our case, the oxidative addition of the alkyne (i.e. the formation of intermediate C) is supposed to be forced by the presence of a coordinative vacancy at the adjacent metal atom, which in turn results from UV-induced CO dissociation. At this point it is interesting to recall that when solvents with coordinative ability higher than that of toluene (e.g. MeCN, Me$_2$CO) are used, yields of complexes 4 increase at the expense of complexes 5. This is explained by assuming that the solvent is able to occupy momentarily any coordination vacancy resulting from CO disociation, thus precluding the C–H addition of the alkyne, whereas not affecting directly

the 1,2-hydrogen shift process which, by defect, becomes dominant.

The pathway eventually leading to the furanylidene complexes 7 obviously requires more steps. A plausible initial step would be a CO insertion into a metal–carbon-(alkyne) bond giving a dimetallacyclopentenone ring $\overline{\text{Mn—CH=CR—C(O)—Mn}}$ (D in Scheme VI), examples of which have been described previously.[3,12,28] Further CO insertion could yield a dimetallacyclohexenedione ring $\overline{\text{Mn—C(O)—CH=CR—C(O)—Mn}}$ (E in Scheme VI), examples of which have been also reported.[29] Reorganization of the latter six-membered ring could finally originate the five-membered 4-oxo-2-furanylidene ligand present in 7. Analogous alkyne coupling with two CO molecules has been reported to occur upon carbonylation of $[\text{Co}_2(\mu\text{-}\text{CRCR'})(\text{CO})_6]$ complexes.[30] In those cases, however, the furanylidene ligands bind the dicobalt moiety in an μ_2,η^1,η^1-fashion (2-electron donor), just as in our complexes 8. The binding mode of the furanylidene ligand in 7, providing a total of 6 electrons to the dimetal center is, to our knowledge, unprecedented.

4.5. Stereochemical Nonrigidity of Complexes 3, 5, and 7. The hydrido–vinyl complex $[\text{Mn}_2(\mu\text{-H})(\mu_2,\eta^1,\eta^2\text{-}\text{CH=CH}_2)(\text{CO})_6(\mu\text{-dppm})]$ (3a) is fluxional at room temperature. Thus, although the room-temperature ^1H or $^{13}\text{C}\{^1\text{H}\}$ NMR spectra would be consistent with an static μ_2,η^1,η^2-vinyl ligand (Table I), the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is not, as it presents a single resonance at 61.9 ppm, therefore suggesting that a dynamic process effectively equalizes the magnetic environment around both phosphorus atoms of the dppm ligand. When the temperature is lowered, this process slows down so as to allow at −50 °C the detection of the static structure, which gives rise to the expected AB pattern in the spectrum. This dynamic process must be similar to those found in other μ_2,η^1,η^2-vinyl complexes, particularly in related dirhenium and triosmium species.[31]

It is worth mentioning that the other μ_2,η^1,η^2-vinyl complex reported in this work, $[\text{Mn}_2(\mu\text{-H})(\mu_2,\eta^1,\eta^2\text{-CPh}=\text{CH}_2)(\text{CO})_6(\mu\text{-dppm})]$ (3b), appears to be stereochemically rigid on the NMR time scale. In a recent work[32] on the stereochemical and dynamic behavior of some diruthenium μ^2,η^1,η^2-vinyl complexes, the stereochemical rigidity of a μ_2,η^1,η^2-CPh=CH$_2$ ligand has been attributed to the lack of a phenyl group on the β-carbon which is expected to relieve, by tautomerism, the electron deficiency generated in the transition state. Such arguments cannot be used in our system, since they would lead to the conclusion that complex 3a should be rigid, which it is not. It is then likely that steric constraints in compound 3b are responsible for its stereochemical rigidity. Those would follow from the presence of the relatively bulky phenyl ring at the α-carbon of the vinyl ligand in 3b.

More uniform is the dynamic behavior of the hydrido–

Table III. Approximate Energy Barrier for Nonrigidity Processes in Complexes 7[a]

compd	δ, ppm	T_c, K	$\Delta\nu$, Hz	ΔG_{T_c}*, kJ mol^{-1}
7a	80.6	193 ± 2	560	35.1 ± 0.4
7a	44.9	203 ± 2	1460	35.4 ± 0.4
7d	79.4	193 ± 2	508	35.3 ± 0.4
7d	45.3	203 ± 2	1439	35.4 ± 0.4

[a] The approximate energy barrier is calculated according to a modified Eyring equation[34] (see text).

alkynyl complexes $[\text{Mn}_2(\mu\text{-H})(\mu_2,\eta^1,\eta^2\text{-C}_2\text{R})(\text{CO})_6(\mu\text{-dppm})]$ (5), as all of them are fluxional in solution. Thus their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra exhibit a single resonance at ca. 52 ppm (Table I) instead of the AB or AX pattern expected for the asymmetric structure found in the solid state for $[\text{Mn}_2(\mu\text{-H})(\mu_2,\eta^1,\eta^2\text{-C}_2\text{Ph})(\text{CO})_6(\mu\text{-dppm})]$ (5b). The dynamic process equalizing both metal environments must be very similar to the one operating in related dirhenium and triosmium μ_2,η^1,η^2-alkynyl complexes,[19,33] i.e. a pivoting movement of the β-carbon of the alkynyl ligand between both metal centers. This movement appears to be particularly fast for compounds 5a–d, as the single ^{31}P resonance shows no sign of splitting down to −90 °C even for the bulkier alkynyl ligand (complex 5c). This is in contrast with the fact that for the closely related rhenium complex $[\text{Re}_2(\mu\text{-H})(\mu_2,\eta^1,\eta^2\text{-C}_2\text{H})(\text{CO})_6(\mu\text{-dppm})]$ a nonaveraged ^{13}C NMR spectrum could be obtained at −77 °C, (coalescence at −46 °C)[19] and this difference is probably a consequence of the weaker alkynyl to metal binding in our dimanganese compounds when compared with their rhenium analogues.

The compounds $[(\text{CO})_4\text{Mn}(\mu\text{-dppm})\{\mu_2,\eta^1,\eta^4\text{-C—CH=}\text{CRC(O)O}\}\text{Mn(CO)}_2]$ (7) also display stereochemical nonrigidity. This is evident from the variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these complexes; thus, their room-temperature spectra exhibit an AX pattern, itself consistent with the solid-state structure determined for 7d by the X-ray study. However, when the temperature is lowered, each of the doublets collapses and eventually splits into two doublets of about the same intensity (Table III). The coalescence temperature for the doublet at ca. 80 ppm is lower than that for the doublet at ca. 45 ppm, but the values of ΔG_{T_c}* calculated from the coalescence temperatures and the Eyring equation[34] (Table III) are close enough to be ascribed to a single dynamic process. Thus, it is concluded that both 7a and 7b exist in solution as mixtures of two conformers in an approximate 1:1 ratio. They strongly differ in the magnetic environments around the phosphorus atoms and probably are the result of different conformations of the six-membered ring formed by the metal atoms, the diphosphine backbone, and the bridging carbene-like atom of the furanylidene ligand.

4.6. Summary. This study reports the preparation of the novel unsaturated dihydride $[\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\mu\text{-dppm})]$ (1) and the reactions of 1 and $[\text{Mn}_2(\text{CO})_8(\mu\text{-dppm})]$ (2) with 1-alkynes which yield hydrido–alkenyl (3), alkenylidene (4 and 6), hydrido–alkynyl (5), and furanylidene (7 and 8) dimanganese compounds; much higher selectivity is achieved using the unsaturated 1 instead of 2, although no furanylidene complexes can be obtained via the hydride 1. The spontaneous transformation of 4b,c into 5b,c complexes provides the first example of a vinylidene to hydrido–alkynyl isomerization, while the reverse transformation can be induced through a deprotonation–protonation sequence. Finally, the furanylidene ligand is found

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Table IV. Experimental Data for the X-ray Diffraction Study on the Complexes 4c, 5b, 6, 7d, and 8d

	4c	5b	6	7d	8d
molecular formula	$C_{37}H_{32}Mn_2O_6P_2$	$C_{39}H_{28}Mn_2O_6P_2$	$C_{35}H_{26}Mn_2O_8P_2$	$C_{37}H_{28}Mn_2O_9P_2$	$C_{38}H_{28}Mn_2O_{10}P_2 \cdot C_4H_8O$
mol wt	744.48	764.47	746.41	788.45	888.56
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Mo Kα radiation (λ = 0.710 73 Å)	niobium-filtered	graphite-monochromated	graphite-monochromated	graphite-monochromated	graphite-monochromated
a, Å	18.671 (8)	20.485 (5)	15.311 (8)	9.704 (4)	12.356 (5)
b, Å	17.390 (8)	17.383 (4)	12.315 (6)	20.071 (8)	14.302 (5)
c, Å	10.966 (6)	10.366 (3)	17.827 (4)	18.216 (8)	12.281 (4)
α, deg	90	90	90	90	74.62 (2)
β, deg	95.66 (2)	100.69 (2)	95.75 (1)	91.98 (2)	77.46 (2)
γ, deg	90	90	90	90	89.81 (2)
V, Å^3	3543 (3)	3627 (2)	3344 (3)	3546 (3)	2039 (1)
Z	4	4	4	4	2
D_{calcd}, g cm^{-3}	1.396	1.400	1.482	1.477	1.447
$F(000)$	1528	1560	1520	1608	912
cryst size, mm	0.15 × 0.18 × 0.22	0.17 × 0.25 × 0.27	0.20 × 0.24 × 0.30	0.17 × 0.24 × 0.28	0.20 × 0.22 × 0.30
μ(Mo Kα), cm^{-1}	8.15	7.98	8.68	8.24	7.28
diffractometer	Siemens AED	CAD 4 Enraf Nonius	Philips PW 1100	Philips PW 1100	Philips PW 1100
scan type	$\theta/2\theta$	$\omega/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	3–12	<3.3	3–12	3–12	3–12
2θ range, deg	5–46	6–54	6–48	6–46	6–48
no. of reflns measd	±h,k,l	±h,k,l	±h,k,l	±h,k,l	±h,k,l
no. of std reflns	one measd after 50 reflns	one measd after 200 reflns	one measd after 50 reflns	one measd after 50 reflns	one measd after 50 reflns
no. of unique tot. data	5150	8108	5680	5131	6858
no. of unique obsd data	990 [$I > 2\sigma(I)$]	3683 [$I > 3\sigma(I)$]	3421 [$I > 2\sigma(I)$]	2697 [$I > 2\sigma(I)$]	2870 [$I > 2\sigma(I)$]
R	0.0594	0.0383	0.0345	0.0467	0.0527
R_w	0.0736	0.0548	0.0441	0.0647	0.0711

to bind the dimanganese centers, either in a μ_2,η^1,η^1-(compound 8) or μ_2,η^1,η^4-fashion (compound 7), this coordination mode of a furanylidene ligand having no precedent in the literature.

5. Experimental Section

5.1. General Considerations. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Photochemical reactions were performed by irradiation with an Applied Photophysics 400-W mercury lamp using jacketed Pyrex vessels refrigerated by a closed 2-propanol circuit kept at −20 °C with a Haake F-3 machine. Solvents were purified according to standard literature procedures[35] and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 60–65 °C. 1-Alkynes were purchased from Aldrich and used as received except for $HC_2CH_2OCH_3$, which was prepared according to a literature procedure,[36] and acetylene which was supplied by SEO and purified by passing through H_2SO_4, a saturated aqueous solution of $NaHSO_3$, H_2SO_4, and KOH train device. Bis(diphenylphosphino)methane[37] and [$Mn_2(CO)_8(\mu$-dppm)][24] were also prepared by literature methods. Alumina for column chromatography was deactivated by appropriate addition of water under nitrogen to the commercial material (Aldrich, neutral, activity 1). Infrared spectra were recorded on a Perkin-Elmer 1720-X infrared Fourier transform spectrometer. Proton, carbon, and phosphorus magnetic resonance spectra (NMR) were measured in a Bruker AC-300 instrument at 300.13, 75.5, and 121.5 MHz, respectively. Chemical shifts are referred to internal TMS (^{1}H, ^{13}C) or external 85% H_3PO_4 aqueous solution. ^{13}C NMR assignments were routinely supported on standard DEPT experiments.[38] Elemental C and H analyses were obtained with a Perkin-Elmer 240 B microanalyzer.

5.2. Preparation of [$Mn_2(\mu$-Cl)$_2(\mu$-dppm)(CO)$_6$]. This complex was prepared through a modification of our previous method.[21] A solution of [$Mn_2(CO)_8(\mu$-dppm)] (2) (1 g, 1.39 mmol) in CH_2Cl_2 (20 mL) was treated at −15 °C with a saturated solution

of Cl_2 in CCl_4 (3.5 mL) to give [$Mn_2Cl_2(CO)_8(\mu$-dppm)]. The solvent and the excess of Cl_2 were removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 (20 mL) and filtered through Celite; the resulting solution was stirred for 3 weeks at 0 °C, while N_2 was bubbled through it. Removal of the solvent yielded 0.930 g of the product (91%), which did not require further purification.

5.3. Preparation of [$Mn_2(\mu$-H)$_2$(CO)$_6(\mu$-dppm)] (1). A solution of [$Mn_2(\mu$-Cl)$_2(\mu$-dppm)(CO)$_6$] (0.450 g, 0.61 mmol) in tetrahydrofuran (50 mL) was treated at 0 °C with Li(HBEt$_3$) (2.5 mL of a 1 M solution in thf, 2.5 mmol) for 1.5 h. Degassed water (1 mL) was then added to the resulting dark green solution (gas evolution occurs), and solvents were removed in vacuum. The deep red resulting residue was extracted with toluene (4 × 15 mL) and filtered through alumina (activity II, 5 × 2.5 cm). The red filtrate was then concentrated in vacuum and gave, after addition of petroleum ether (30 mL) and crystallization at −20 °C for 1 day, red purple crystals of 1·(toluene) (0.310 g, 67%). Anal. Calcd for $C_{38}H_{32}O_6P_2Mn_2$ (1·C_7H_8): C, 60.33; H, 4.26. Found: C, 60.14; H, 4.22.

5.4. Preparation of [$Mn_2(\mu$-η^1,η^2-CH=CH$_2$)(CO)$_6(\mu$-dppm)] (3a). Acetylene was bubbled through a solution of compound 1·(toluene) (0.150 g, 0.20 mmol) in tetrahydrofuran (20 mL) at room temperature for 24 h. Solvents were removed in vacuum from the yellow resulting solution, and the residue was chromatographied through an alumina column (activity IV, 11 × 2.5 cm). Elution with petroleum ether–toluene (10:1) gave a yellow band which yielded, after removal of solvent in vacuum, compound 3a as a microcrystalline powder (0.100 g, 65%). Recrystallization from tetrahydrofuran–petroleum ether yielded crystals of the compound as a tetrahydrofuran solvate. Elution with petroleum ether–toluene (10:2) gave an orange fraction containing very small amounts of unidentified species (<3%). Anal. Calcd for C_{37}-$H_{34}O_7P_2Mn_2$ (3a·C_4H_8O): C, 58.26; H, 4.48. Found: C, 58.27; H, 4.51.

5.5. Preparation of [$Mn_2(\mu$-H){μ-η^1,η^2-C(Ph)=CH$_2$}(CO)$_6$-(μ-dppm)] (3b). Compound 1·(toluene) (0.150 g, 0.20 mmol) and HC_2Ph (1 mL, 9.1 mmol) were stirred at room temperature for 3 days. Solvents were then removed in vacuum, and the residue was washed with petroleum ether (3 × 10 mL) yielding reasonably pure complex 3b as a yellow powder (0.105 g, 68%). Analytically pure samples of this complex could only be obtained in small amounts, as it slowly decomposes during crystallization even at −20 °C. Anal. Calcd for $C_{39}H_{30}O_6P_2Mn_2$ (3b): C, 61.12; H, 3.94. Found: C, 61.03; H, 4.11.

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5.6. Reaction of Compound 1 with HC₂ᵗBu. Compound 1·(toluene) (0.260 g, 0.34 mmol) and HC₂ᵗBu (1.0 mL, 8.0 mmol) were stirred in tetrahydrofuran (25 mL) at room temperature for 3 days, affording an orange solution. Solvent was then removed under vacuum, and the residue was chromatographed on an alumina column (activity IV, 11 × 2.5 cm) at -40 °C. A yellow fraction was collected by elution with petroleum ether which yielded, after removal of solvents under vacuum, compound **5c** as a yellow powder (0.044 g, 17%). Elution with petroleum ether–toluene (5:2) gave a red fraction which yielded similarly compound **4c** (0.098 g, 39%). Room-temperature chromatography of the same reaction mixture gave higher yields of **5c** at the expense of **4c**, typically 36% for **5c** and 15% for **4c**. Analogous effects were observed when longer reaction times were used. Anal. Calcd for C₃₇H₃₂O₆P₂Mn₂ (**4c** or **5c**): C, 59.69; H, 4.33. Found for **4c**: C, 59.90; H, 4.36. Found for **5c**: C, 59.92; H, 4.36.

5.7. Preparation of [(CO)₃Mn(μ-dppm){μ-C=CH—C-(O)OMe}Mn(CO)₃] (6). A mixture of compound 1·(toluene) (0.090 g, 0.12 mmol) and HC₂CO₂Me (0.7 mL, 7.9 mmol) in tetrahydrofuran was stirred at room temperature for 1 week. Solvent was then removed under vacuum, and the resulting orange residue was chromatographed on an alumina column (activity IV, 11 × 2.5 cm) at room temperature. Elution with petroleum ether–toluene (10:3) gave an orange band which yielded, after removal of the solvent under vacuum, compound **6** as an orange powder (0.035 g, 39%). Further elution with petroleum ether–toluene (1:1) gave a blue fraction containing trace amounts of unidentified species. Anal. Calcd for C₃₅H₂₆O₈P₂Mn₂ (**6**): C, 56.32; H, 3.51. Found: C, 56.52; H, 3.57.

5.8. Photochemical Reactions of Compound 2 with C₂H₂.
(a) In Toluene. A solution of compound **2** (0.400 g, 0.56 mmol) in toluene (50 mL) was irradiated at -20 °C while C₂H₂ was bubbled through it. After 14 h, the solvent was removed under vacuum and the red-brown residue was chromatographed on an alumina column (activity IV, 14 × 2.5 cm). Elution with petroleum ether gave two not completely resolved yellow bands. The first one contained unreacted starting material, whereas recrystallization of the second fraction from toluene–petroleum ether yielded pure compound **5** as yellow crystals (0.025 g, 6%). Elution with petroleum ether–toluene (1:1) gave a yellow fraction containing mostly [Mn₂(μ-η¹,η²-CO)(CO)₄(μ-dppm)₂]. Further elution with pure toluene gave a violet fraction which yielded pure compound **8a** in very small amounts (<1%). Finally, elution with petroleum ether–tetrahydrofuran (10:2) gave an orange fraction which yielded, after removal of solvents under vacuum, compound **7a** as an orange powder (0.080 g, 19%). Anal. Calcd for C₃₃H₂₄O₆P₂Mn₂ (**5a**): C, 57.58; H, 3.51. Found: C, 57.48; H, 3.54. Calcd for C₃₅H₂₄O₈P₂Mn₂ (**7a**): C, 56.47; H, 3.25. Found: C, 56.68; H, 3.28.

(b) In Toluene under CO Atmosphere. The preceding reaction was carried out under the same conditions except that CO bubbling through the solution was maintained simultaneously with that of C₂H₂. The products obtained after similar workup were the same although yields changed moderately: **5a** 0.020 g, 5%; **8a**: 0.008 g, 2%; **7a** 0.0065 g, 16%. Anal. Calcd for C₃₆H₂₄O₉P₂Mn₂ (**8a**): C, 55.98; H, 3.13. Found: C, 56.14; H, 3.15.

5.9. Photochemical Reactions of Compound 2 with HC₂Ph.
(a) In Toluene. A solution of compound **2** (0.300 mg, 0.42 mmol) and HC₂Ph (1.0 mL, 9.1 mmol) in toluene (30 mL) was irradiated at -20 °C for 28 h. After removal of the solvent, the red residue was chromatographed on an alumina column (activity IV, 11 × 2.5 cm). Once unreacted **2** was removed by elution with petroleum ether, elution with petroleum ether–toluene (10:2) gave a yellow fraction which yielded complex **5b** as a yellow powder (0.150 g, 47%). Further elution with pure CH₂Cl₂ gave another yellow fraction which yielded 0.01 g of the mononuclear complex *fac*-[Mn(C₂Ph)(CO)₃(dppm)] previously prepared in our laboratory.[23] Anal. Calcd for C₃₉H₂₈O₆P₂Mn₂ (**5b**): C, 61.27; H, 3.69. Found: C, 61.30; H, 3.65.

(b) In Acetonitrile. A solution of compound **2** (0.150 mg, 0.21 mmol) and HC₂Ph (0.5 mL, 4.5 mmol) in acetonitrile (30 mL) was irradiated at -20 °C for 2.5 h. After removal of the solvent, the red residue was chromatographed on an alumina column (activity IV, 7 × 2.5 cm) at -40 °C. Elution with petroleum ether–toluene (5:1) gave a yellow fraction, which yielded *fac*-[Mn(H)(CO)₃-

atom	x/a	y/b	z/c	U
Mn(1)	1099 (2)	2209 (2)	1898 (3)	38 (2)[a]
Mn(2)	-321 (2)	2648 (2)	1163 (4)	45 (2)[a]
P(1)	771 (4)	1395 (4)	3384 (6)	36 (3)[a]
P(2)	-814 (4)	1889 (4)	2590 (6)	41 (3)[a]
O(1)	1623 (10)	3207 (11)	22 (18)	77 (7)
O(2)	2519 (10)	2429 (10)	3306 (16)	75 (6)
O(3)	1316 (11)	851 (12)	332 (19)	85 (7)
O(4)	30 (10)	3408 (11)	-1101 (19)	84 (7)
O(5)	-1743 (11)	3388 (12)	641 (19)	93 (7)
O(6)	-290 (9)	1257 (11)	-399 (17)	73 (6)
C(1)	1413 (14)	2800 (17)	746 (26)	67 (9)
C(2)	1952 (16)	2321 (17)	2759 (26)	71 (9)
C(3)	1218 (15)	1369 (18)	962 (26)	66 (9)
C(4)	-77 (14)	3123 (15)	-135 (28)	59 (9)
C(5)	-1159 (16)	3056 (16)	847 (26)	72 (10)
C(6)	-314 (13)	1829 (17)	202 (25)	53 (8)
C(7)	499 (12)	2926 (13)	2322 (20)	37 (7)
C(8)	11 (13)	3498 (15)	2635 (22)	49 (8)
C(9)	171 (13)	4359 (14)	2543 (23)	44 (7)
C(10)	591 (17)	4615 (17)	3774 (28)	92 (11)
C(11)	631 (15)	4595 (17)	1591 (25)	74 (11)
C(12)	-557 (18)	4798 (18)	2381 (29)	98 (11)
C(13)	1237 (11)	471 (12)	3388 (19)	24 (6)
C(14)	1938 (13)	453 (15)	4015 (22)	49 (8)
C(15)	2318 (15)	-250 (19)	3991 (26)	80 (10)
C(16)	1999 (16)	-918 (18)	3434 (26)	74 (9)
C(17)	1311 (18)	-879 (18)	2860 (28)	88 (10)
C(18)	931 (13)	-185 (16)	2835 (23)	53 (8)
C(19)	938 (12)	1688 (15)	4978 (22)	47 (8)
C(20)	839 (14)	1148 (16)	5906 (27)	65 (9)
C(21)	918 (14)	1349 (19)	7135 (28)	76 (10)
C(22)	1134 (15)	2115 (19)	7429 (27)	85 (10)
C(23)	1247 (14)	2687 (18)	6544 (27)	76 (9)
C(24)	1131 (12)	2456 (14)	5281 (22)	49 (8)
C(25)	-189 (11)	1143 (13)	3221 (20)	35 (7)
C(26)	-1598 (13)	1315 (16)	2044 (25)	59 (8)
C(27)	-1889 (15)	775 (16)	2905 (25)	65 (9)
C(28)	-2447 (18)	281 (18)	2422 (31)	78 (9)
C(29)	-2718 (15)	336 (17)	1247 (29)	73 (10)
C(30)	-2468 (16)	789 (18)	377 (27)	75 (10)
C(31)	-1880 (14)	1330 (16)	746 (25)	59 (8)
C(32)	-1168 (12)	2371 (14)	3896 (21)	40 (7)
C(33)	-776 (13)	2423 (15)	5064 (24)	55 (8)
C(34)	-1071 (15)	2917 (17)	5965 (26)	76 (10)
C(35)	-1709 (17)	3308 (17)	5676 (29)	79 (10)
C(36)	-2059 (15)	3259 (18)	4578 (28)	74 (10)
C(37)	-1795 (14)	2792 (16)	3652 (23)	60 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(dppm)] (15 mg). Further elution with petroleum ether–toluene (2:1) gave a red fraction containing **4b**. Recrystallization of the product from toluene–petroleum ether gave red crystals of **4b** (0.040 g, 25%). Anal. Calcd for C₃₉H₂₈O₉P₂Mn₂ (**4b**): C, 61.27; H, 3.69. Found: C, 61.28; H, 3.72.

5.10. Photochemical Reactions of Compound 2 with HC₂ᵗBu. **(a) In Toluene.** A solution of compound **2** (0.300 g, 0.42 mmol) and HC₂ᵗBu (1 mL, 8.0 mmol) in toluene (30 mL) was irradiated at -20 °C for 24 h. After removal of the solvent, the resulting orange residue was chromatographed on an alumina column (activity IV, 11 × 2.5 cm) at -40 °C. Elution with petroleum ether gave a yellow fraction which yielded, after removal of solvents in vacuum, compound **5c** (0.030 g, 10%). Elution with petroleum ether–toluene (10:3) gave a red fraction yielding similarly **4c** (0.085 g, 27%). Further elution with toluene and CH₂Cl₂ gave respectively yellow and orange fractions containing the previously known complexes [Mn₂(CO)₆(dppm)₂] (0.030 g, 7%) and [Mn₂(μ-η¹,η²-CO)(CO)₄(μ-dppm)₂] (0.050 g, 12%).

(b) In Acetone. A solution of **2** (0.300 g, 0.42 mmol) and HC₂ᵗBu (1 mL, 8.0 mmol) in acetone (30 mL) was irradiated at -20 °C for 10 h. Solvent was then removed under vacuum, and the residue was dissolved in tetrahydrofuran and filtered through Celite. Crystallization from tetrahydrofuran–petroleum ether at

Table VI. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³) with Esd's in Parentheses for the Non-Hydrogen Atoms of 5b[a]

atom	x/a	y/b	z/c	U_{eq}
Mn(1)	2828 (1)	545 (1)	4189 (1)	47.0 (3)
Mn(2)	1514 (1)	1054 (1)	4439 (1)	44.9 (3)
P(1)	3312 (1)	1677 (1)	5059 (1)	44.8 (4)
P(2)	1944 (1)	2237 (1)	5350 (1)	45.1 (4)
O(1)	2322 (3)	-934 (3)	3006 (5)	82 (2)
O(2)	4049 (3)	-252 (4)	5379 (7)	121 (3)
O(3)	3223 (3)	918 (4)	1668 (5)	105 (3)
O(4)	885 (3)	1757 (4)	1948 (5)	107 (3)
O(5)	323 (2)	1304 (3)	5576 (5)	83 (2)
O(6)	887 (3)	-363 (4)	3275 (7)	117 (3)
C(1)	2488 (4)	-354 (4)	3467 (5)	60 (2)
C(2)	3572 (4)	61 (4)	4910 (7)	71 (3)
C(3)	3082 (4)	773 (4)	2659 (6)	64 (2)
C(4)	1140 (4)	1509 (4)	2937 (6)	66 (2)
C(5)	794 (3)	1212 (4)	5170 (6)	55 (2)
C(6)	1154 (4)	167 (4)	3713 (7)	67 (3)
C(7)	2342 (3)	409 (3)	5621 (5)	47 (2)
C(8)	1942 (3)	278 (3)	6341 (5)	49 (2)
C(9)	1648 (3)	-8 (3)	7425 (5)	56 (2)
C(10)	1000 (4)	-260 (5)	7242 (9)	85 (3)
C(11)	744 (5)	-521 (6)	8317 (12)	113 (4)
C(12)	1141 (7)	-531 (5)	9553 (10)	114 (6)
C(13)	1782 (6)	-307 (5)	9710 (8)	107 (4)
C(14)	2036 (5)	-34 (5)	8650 (7)	82 (3)
C(15)	3988 (3)	2027 (3)	4293 (6)	56 (2)
C(16)	4596 (4)	1682 (6)	4610 (11)	115 (5)
C(17)	5113 (4)	1922 (6)	4002 (11)	140 (5)
C(18)	5037 (4)	2492 (5)	3141 (10)	95 (4)
C(19)	4439 (4)	2827 (4)	2805 (8)	76 (3)
C(20)	3917 (4)	2602 (4)	3373 (7)	63 (2)
C(21)	3680 (3)	1732 (4)	6792 (6)	61 (2)
C(22)	4055 (5)	2363 (5)	7262 (9)	109 (4)
C(23)	4305 (6)	2441 (8)	8577 (11)	145 (6)
C(24)	4182 (5)	1869 (8)	9431 (9)	129 (5)
C(25)	3823 (4)	1238 (7)	8979 (7)	99 (4)
C(26)	3575 (3)	1164 (5)	7647 (6)	69 (3)
C(27)	2723 (3)	2482 (3)	4834 (6)	47 (2)
C(28)	2112 (3)	2381 (3)	7116 (5)	55 (2)
C(29)	2508 (4)	2976 (5)	7697 (8)	93 (3)
C(30)	2599 (6)	3094 (6)	9026 (9)	123 (5)
C(31)	2300 (5)	2647 (6)	9799 (8)	110 (5)
C(32)	1900 (4)	2044 (4)	9253 (7)	84 (3)
C(33)	1806 (3)	1920 (4)	7907 (6)	58 (2)
C(34)	1434 (2)	3086 (2)	4769 (4)	58 (2)
C(35)	1377 (2)	3334 (3)	3488 (6)	77 (2)
C(36)	979 (3)	3964 (3)	3048 (8)	98 (3)
C(37)	648 (4)	4336 (4)	3859 (11)	135 (4)
C(38)	704 (4)	4104 (4)	5148 (10)	141 (4)
C(39)	1096 (3)	3468 (3)	5603 (7)	99 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Thermal Parameters (Å² × 10³) with Esd's in Parentheses for the Non-Hydrogen Atoms of 6[a]

atom	x/a	y/b	z/c	U_{eq}
Mn(1)	11 (1)	960 (1)	1355 (1)	35.6 (2)
Mn(2)	-156 (1)	398 (1)	2921 (1)	40.9 (2)
P(1)	843 (1)	2516 (1)	1685 (1)	36.0 (3)
P(2)	436 (1)	2086 (1)	3288 (1)	37.9 (3)
O(1)	-632 (2)	1994 (2)	-104 (2)	64 (1)
O(2)	-945 (2)	-1089 (2)	951 (2)	67 (1)
O(3)	-1710 (2)	1716 (2)	1744 (2)	59 (1)
O(4)	-568 (3)	-1901 (3)	2610 (2)	107 (2)
O(5)	538 (3)	-477 (3)	4394 (2)	83 (2)
O(6)	-1955 (2)	641 (3)	3388 (2)	92 (2)
O(7)	1097 (2)	375 (2)	869 (1)	43 (1)
O(8)	2372 (2)	-520 (2)	1102 (2)	59 (1)
C(1)	-359 (2)	1590 (3)	448 (2)	42 (1)
C(2)	-556 (3)	-323 (3)	1105 (2)	43 (1)
C(3)	-1003 (3)	1421 (3)	1679 (2)	42 (1)
C(4)	-427 (3)	-993 (4)	2701 (2)	64 (2)
C(5)	273 (3)	-114 (3)	3821 (3)	56 (2)
C(6)	-1259 (3)	607 (3)	3210 (3)	58 (2)
C(7)	731 (2)	225 (3)	2287 (2)	40 (1)
C(8)	1490 (2)	-206 (3)	2100 (2)	47 (1)
C(9)	1644 (3)	-99 (3)	1327 (2)	47 (1)
C(10)	2524 (3)	-381 (4)	322 (3)	66 (2)
C(11)	1829 (2)	2576 (3)	1192 (2)	44 (1)
C(12)	2657 (3)	2325 (4)	1507 (3)	64 (2)
C(13)	3358 (3)	2330 (5)	1063 (4)	90 (2)
C(14)	3219 (4)	2599 (5)	313 (4)	92 (3)
C(15)	2408 (3)	2841 (4)	-8 (3)	78 (2)
C(16)	1724 (3)	2834 (4)	421 (3)	60 (2)
C(17)	404 (2)	3888 (3)	1522 (2)	41 (1)
C(18)	-477 (3)	4073 (3)	1366 (3)	55 (1)
C(19)	-802 (3)	5129 (4)	1288 (3)	71 (2)
C(20)	-238 (3)	5993 (3)	1344 (3)	71 (2)
C(21)	652 (4)	5813 (4)	1486 (3)	79 (2)
C(22)	965 (3)	4778 (3)	1575 (3)	68 (2)
C(23)	1261 (2)	2546 (3)	2681 (2)	39 (1)
C(24)	1098 (2)	2022 (3)	4201 (2)	42 (1)
C(25)	785 (3)	2363 (3)	4856 (2)	58 (2)
C(26)	1255 (4)	2188 (4)	5552 (3)	73 (2)
C(27)	2049 (4)	1698 (4)	5596 (3)	71 (2)
C(28)	2382 (3)	1360 (4)	4948 (3)	81 (2)
C(29)	1912 (3)	1517 (4)	4258 (2)	67 (2)
C(30)	-251 (2)	3297 (3)	3368 (2)	45 (1)
C(31)	-1147 (3)	3241 (3)	3252 (3)	62 (2)
C(32)	-1664 (3)	4152 (4)	3299 (3)	78 (2)
C(33)	-1298 (3)	5132 (4)	3446 (4)	95 (2)
C(34)	-396 (4)	5206 (4)	3548 (4)	119 (3)
C(35)	117 (3)	4298 (4)	3519 (3)	84 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

-20 °C overnight yielded complex 4c as red crystals (0.110 g, 35%), which were easily separated from minute amounts of a contaminating yellow powder (consisting of [Mn₂(CO)₆(dppm)₂] and [Mn₂(μ-η¹,η²-CO)(CO)₄(μ-dppm)₂]) by washing with petroleum ether.

5.11. Photochemical Reactions of Compound 2 with HC₂CH₂OMe. (a) In Toluene. A solution of compound 2 (0.400 g, 0.56 mmol) and HC₂CH₂OMe (1 mL, 11.8 mmol) in toluene (30 mL) was irradiated at -20 °C for 14 h. After removal of the solvent under vacuum, the red brown residue was chromatographed on an alumina column (activity IV, 14 × 2.5 cm). Elution with petroleum ether gave a yellow fraction containing unreacted 2 (0.015 g, 4%). Elution with petroleum ether-toluene (5:2) gave another yellow fraction yielding, after removal of solvents in vacuum, compound 5d, (0.055 g, 13%). Further elution with toluene gave an orange-brown fraction and then a violet one. The first one contained small amounts of a mixture of products, [Mn₂(CO)₆(dppm)₂] and [Mn₂(μ-η¹,η²-CO)(CO)₄(μ-dppm)₂] being identified. The violet fraction yielded, after usual workup, complex 8d as red-violet powder (0.015 g, 3%). Recrystallization from tetrahydrofuran–petroleum ether gave crystals of 8d·thf (as de-

termined by ¹H NMR spectroscopy). Finally, elution with petroleum ether–tetrahydrofuran (5:1) gave an orange fraction, yielding compound 7d as an orange powder (0.075 g, 16%). Recrystallization from toluene–petroleum ether gave crystals of 7d·¹/₂(toluene) (as determined by ¹H NMR spectroscopy). Anal. Calcd for C₃₅H₂₈O₇P₂Mn₂ (5d): C, 57.39; H, 3.85. Found: C, 57.59; H, 3.90. Calcd for C₄₂H₃₆O₁₁P₂Mn₂ (8h·thf): C, 56.78; H, 4.05. Found: C, 56.85; H, 4.07. Calcd for C₄₀.₅H₃₂O₉P₂Mn₂ (7d·¹/₂-(toluene)): C, 58.29; H, 3.86. Found: C, 58.36; H, 3.88. The single crystals of 7d and 8d used for X-ray diffraction studies were both obtained through recrystallizations from Et₂O–petroleum ether at -20 °C and were found to be free of solvents in both cases.

(b) In Toluene under CO Atmosphere. The reaction was carried out as before but with gentle CO bubbling through the solution. The products obtained after similar workup were the same although yields changed moderately: 5d 0.050 g, 12%; 8d·thf 0.028 g, 6%; 7d·¹/₂(toluene) 0.045 g, 10%.

(c) In Acetone. A solution of 2 (0.300 g, 042 mmol) and HC₂CH₂OMe (1 mL, 11.8 mmol) in acetone (20 mL) was irradiated at -20 °C for 8 h. After removal of the solvent under vacuum, the residue was chromatographed on an alumina column at -20 °C (activity IV, 20 × 2.5 cm). Elution with petroleum ether–toluene (1:1) gave a yellow fraction yielding complex 5d (0.010

Table VIII. Fractional Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) with Esd's in Parentheses for the Non-Hydrogen Atoms of 7d

atom	x/a	y/b	z/c	U
Mn(1)	5306 (1)	2760 (1)	2578 (1)	41.4 (5)ᵃ
Mn(2)	2072 (1)	1624 (1)	2104 (1)	41.4 (5)ᵃ
P(1)	4377 (2)	3207 (1)	1473 (1)	36.5 (7)ᵃ
P(2)	2880 (2)	1856 (1)	1012 (1)	37.2 (8)ᵃ
O(1)	7020 (7)	1682 (4)	1948 (4)	66 (3)ᵃ
O(2)	7596 (8)	3737 (4)	2589 (4)	88 (3)ᵃ
O(3)	3744 (9)	3715 (4)	3487 (4)	83 (3)ᵃ
O(4)	6410 (10)	2221 (4)	3975 (4)	102 (4)ᵃ
O(5)	738 (10)	375 (4)	1627 (5)	105 (4)ᵃ
O(6)	-360 (7)	2431 (4)	1767 (5)	96 (4)ᵃ
O(7)	3978 (6)	1398 (3)	2655 (3)	44 (2)ᵃ
O(8)	3227 (7)	444 (3)	3216 (4)	66 (3)ᵃ
O(9)	968 (8)	1292 (4)	4458 (4)	77 (3)ᵃ
C(1)	6327 (10)	2097 (5)	2137 (5)	48 (3)ᵃ
C(2)	6724 (11)	3355 (5)	2552 (5)	56 (4)ᵃ
C(3)	4289 (11)	3366 (5)	3123 (6)	54 (4)ᵃ
C(4)	5964 (11)	2428 (5)	3439 (6)	60 (4)ᵃ
C(5)	1276 (11)	871 (5)	1795 (5)	61 (4)ᵃ
C(6)	597 (10)	2090 (5)	1885 (6)	56 (4)ᵃ
C(7)	3017 (9)	1040 (5)	3111 (5)	48 (4)ᵃ
C(8)	3684 (9)	2113 (4)	2707 (4)	40 (3)ᵃ
C(9)	2496 (9)	2137 (5)	3101 (5)	43 (3)ᵃ
C(10)	1972 (9)	1500 (4)	3267 (5)	43 (3)ᵃ
C(11)	725 (11)	1324 (7)	3683 (6)	62 (5)ᵃ
C(12)	1368 (14)	662 (5)	4708 (8)	80 (6)ᵃ
C(13)	5618 (8)	3535 (4)	825 (4)	38 (2)
C(14)	6977 (9)	3347 (5)	841 (5)	46 (2)
C(15)	7877 (11)	3598 (5)	333 (5)	58 (3)
C(16)	7397 (11)	4045 (5)	-177 (6)	62 (3)
C(17)	6049 (12)	4222 (6)	-226 (6)	63 (3)
C(18)	5154 (11)	3970 (4)	281 (5)	52 (2)
C(19)	3373 (8)	3942 (4)	1707 (4)	38 (2)
C(20)	4076 (10)	4538 (4)	1851 (5)	43 (2)
C(21)	3370 (10)	5073 (5)	2117 (6)	56 (3)
C(22)	1997 (11)	5038 (5)	2262 (6)	64 (3)
C(23)	1288 (12)	4461 (6)	2119 (6)	68 (3)
C(24)	1985 (10)	3910 (5)	1859 (5)	49 (2)
C(25)	3155 (10)	2746 (5)	855 (5)	40 (3)ᵃ
C(26)	1732 (8)	1646 (4)	225 (4)	42 (2)
C(27)	809 (10)	2091 (5)	-94 (6)	64 (3)
C(28)	-74 (12)	1889 (6)	-683 (6)	71 (3)
C(29)	-58 (12)	1260 (6)	-913 (7)	75 (3)
C(30)	810 (12)	796 (6)	-594 (7)	77 (3)
C(31)	1733 (11)	1000 (5)	-32 (6)	66 (3)
C(32)	4459 (8)	1442 (4)	763 (5)	39 (2)
C(33)	4772 (10)	810 (5)	1033 (5)	53 (2)
C(34)	5940 (11)	476 (6)	829 (6)	65 (3)
C(35)	6808 (13)	756 (6)	354 (6)	75 (3)
C(36)	6537 (13)	1380 (6)	81 (7)	80 (3)
C(37)	5367 (9)	1726 (5)	281 (5)	57 (3)

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

Table IX. Fractional Atomic Coordinates (×10⁴) and Isotropic Thermal Parameters (Å² × 10³) with Esd's in Parentheses for the Non-Hydrogen Atoms of 8d

atom	x/a	y/b	z/c	U
Mn(1)	1000 (1)	3066 (1)	1145 (1)	47.3 (6)ᵃ
Mn(2)	2415 (1)	1650 (1)	759 (1)	46.9 (6)ᵃ
P(1)	1826 (2)	3328 (2)	2620 (2)	42.9 (9)ᵃ
P(2)	3407 (2)	1837 (2)	2132 (2)	43.3 (9)ᵃ
O(1)	-1239 (6)	3296 (6)	2500 (7)	98 (4)ᵃ
O(2)	-300 (6)	2828 (6)	-523 (7)	89 (4)ᵃ
O(3)	1359 (6)	5172 (6)	-38 (6)	75 (4)ᵃ
O(4)	103 (5)	1024 (5)	2400 (5)	66 (3)ᵃ
O(5)	2233 (7)	-475 (5)	1848 (6)	88 (4)ᵃ
O(6)	4524 (7)	1655 (7)	-861 (7)	100 (4)ᵃ
O(7)	1328 (7)	1072 (6)	-895 (7)	94 (4)ᵃ
O(8)	3425 (4)	3725 (4)	6 (5)	50 (3)ᵃ
O(9)	4582 (5)	4979 (5)	-1172 (6)	77 (3)ᵃ
O(101)	2502 (20)	4525 (12)	-3564 (13)	90 (5)
O(102)	3023 (23)	4379 (14)	-3793 (18)	47 (8)
C(1)	-368 (8)	3194 (7)	2037 (8)	59 (4)ᵃ
C(2)	227 (8)	2924 (7)	65 (9)	58 (4)ᵃ
C(3)	1222 (7)	4372 (3)	427 (8)	54 (4)ᵃ
C(4)	762 (8)	1641 (7)	1859 (8)	56 (4)ᵃ
C(5)	2304 (8)	352 (8)	1463 (8)	58 (4)ᵃ
C(6)	3703 (8)	1649 (7)	-209 (8)	60 (4)ᵃ
C(7)	1719 (8)	1349 (7)	-266 (9)	62 (5)ᵃ
C(8)	2534 (7)	3095 (7)	-68 (7)	47 (3)ᵃ
C(9)	3848 (8)	4366 (7)	-1061 (8)	57 (4)ᵃ
C(10)	3250 (8)	4169 (7)	-1867 (8)	56 (4)ᵃ
C(11)	2502 (7)	3434 (6)	-1292 (7)	50 (4)ᵃ
C(12)	3494 (10)	4785 (9)	-3111 (11)	91 (4)
C(13)	2169 (29)	5128 (21)	-4425 (27)	134 (13)
C(132)	2914 (45)	5030 (30)	-4896 (33)	146 (18)
C(14)	3272 (6)	3015 (6)	2448 (8)	43 (4)ᵃ
C(15)	4917 (7)	1742 (7)	1673 (7)	48 (4)ᵃ
C(16)	5662 (8)	2528 (8)	1327 (8)	64 (5)ᵃ
C(17)	6779 (8)	2398 (9)	966 (10)	84 (6)ᵃ
C(18)	7140 (10)	1496 (10)	936 (10)	83 (6)ᵃ
C(19)	6394 (8)	706 (9)	1285 (9)	72 (5)ᵃ
C(20)	5281 (8)	828 (8)	1662 (8)	65 (5)ᵃ
C(21)	3083 (7)	1011 (6)	3595 (7)	48 (4)ᵃ
C(22)	3837 (8)	926 (7)	4295 (8)	62 (5)ᵃ
C(23)	3553 (9)	373 (8)	5436 (9)	71 (5)ᵃ
C(24)	2509 (9)	-108 (7)	5904 (9)	67 (5)ᵃ
C(25)	1748 (8)	-24 (7)	5209 (8)	63 (5)ᵃ
C(26)	2022 (8)	519 (6)	4059 (8)	52 (4)ᵃ
C(27)	1216 (8)	2711 (6)	4159 (7)	46 (4)ᵃ
C(28)	1793 (8)	2777 (7)	4984 (8)	57 (4)ᵃ
C(29)	1380 (9)	2320 (8)	6131 (9)	66 (5)ᵃ
C(30)	376 (9)	1806 (8)	6495 (9)	66 (5)ᵃ
C(31)	-220 (8)	1769 (7)	5669 (8)	63 (4)ᵃ
C(32)	208 (8)	2214 (7)	4516 (8)	57 (4)ᵃ
C(33)	1860 (8)	4592 (7)	2641 (8)	48 (4)ᵃ
C(34)	2793 (10)	5229 (7)	2052 (10)	68 (5)ᵃ
C(35)	2745 (10)	6191 (8)	2048 (10)	72 (5)ᵃ
C(36)	1842 (11)	6545 (9)	2594 (9)	78 (6)ᵃ
C(37)	892 (12)	5923 (9)	3189 (11)	89 (6)ᵃ
C(38)	930 (9)	4955 (8)	3200 (9)	70 (5)ᵃ
C(39)	5158 (15)	2843 (13)	4808 (16)	137 (6)
C(40)	6099 (18)	2565 (15)	4393 (18)	151 (7)
C(41)	6623 (20)	2183 (17)	5343 (24)	202 (9)
C(42)	5836 (23)	1999 (18)	6393 (22)	202 (9)
C(43)	4846 (22)	2624 (19)	6030 (24)	209 (10)

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U$_{ij}$ tensor.

g, 3%). Elution with petroleum ether–toluene (2:3) gave an orange fraction and then a violet one. The first one yielded complex **4d** as a reasonably pure orange powder (0.150 g, 45%) and the second one yielded complex **8d** (0.010 g, 3%). Finally, elution with petroleum ether–tetrahydrofuran (5:1) gave an orange fraction yielding compound **7d** (0.040 g, 12%). Compound **4d** can be recrystallized from toluene–petroleum ether at -20 °C, yielding red crystals of the pure compound, although this is accompanied by appreciable decomposition. Anal. Calcd for C₃₅H₂₈O₇P₂Mn₂ (**4d**): C, 57.39; H, 3.85. Found: C, 57.16; H, 3.80.

5.12. Preparation of Alkenylidene Complexes from Their Hydrido–Alkynyl Isomers. The procedure will be exemplified with the preparation of compound **4b**: To a solution of compound **5b** (0.100 g, 013 mmol) in tetrahydrofuran (15 mL), solid Li(AlH₄) was slowly added at room temperature until gas evolution from the solution ceased (ca. 0.010 g). This was accompanied by a color change from yellow to brown. Then, an excess of a 1 M solution of HBF₄ in Et₂O (ca. 0.5 mL) was added to the solution, which caused more gas evolution and a color change from brown to red. Toluene (20 mL) and water (20 mL) were then added. The red

layer was afterwards collected, washed with 3 × 20 mL of H₂O, dried over anhydrous MgSO₄, and filtered through Celite. Crystallization of the filtrate by addition of petroleum ether and storing overnight at -20 °C yielded compound **4b** as red crystals (0.060 g, 60%). In a similar way, compound **4c** was obtained in 62% yield from compound **5c**.

5.13. X-ray Data Collection, Structure Determination, and Refinement for 4c, 5b, 6, 7d, and 8d. The crystallographic data for the five compounds are summarized in Table IV. All crystals of **4c** were of small size and of poor quality. The selected crystal diffracted rather weakly, so that only 20% of observed reflections could be obtained. Intensity data for the five crystals were

collected at room temperature, and the individual profiles have been analyzed following Lehmann and Larsen.[39] Intensities were corrected for Lorentz and polarization effects. No correction for absorption was necessary.

All structures were solved by Patterson and Fourier methods and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters for all non-hydrogen atoms (5b and 6), for all non-hydrogen atoms except the carbon atoms of the phenyl rings (7d), for all non-hydrogen atoms except the carbon and oxygen atoms of the methoxymethyl substituent (which was found disordered and distributed in two positions of equal occupancy factors) and the atoms of the tetrahydrofuran of solvation (which were treated all as carbon atoms) (8d), and for only the Mn and P atoms (4c). All the hydrogen atoms of 6 and 7d were clearly located in the final ΔF map and refined isotropically; those of 4c, 5b (except the hydride, clearly located), and 8d (except those of the disordered methoxymethyl substituent and of the solvent molecule) were placed at their geometrically calculated positions and refined "riding" the corresponding carbon atoms. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 40. All calculations were carried out on the CRAY X-MP/12 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the GOULD POWERNODE

6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs.[41] The final atomic coordinates for the non-hydrogen atoms are given in Tables V (4c), VI (5b), VII (6), VIII (7d), and IX (8d).

Supplementary Material Available: Listings of hydrogen coordinates and thermal parameters (Tables SI–SV), thermal parameters (Tables SVI–SX), and bond distances and angles (Tables XI–XV) (32 pages); listings of observed and calculated structure factors (77 pages). Ordering information is given on any current masthead page.

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Metal-Induced 1,5- and 1,4-Hydrogen Shifts in Polysubstituted Butadienyl Units η³-Bonded to Palladium†

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3-Hexyne (2 equiv) is readily inserted into the Pd–C bond of the cyclopalladated compound derived from the ((dimethylamino)methyl)ferrocene ligand, affording a kinetic isomer, 2. The latter may be isomerized into a thermodynamic isomer 3 in pyridine at 100 °C. Two further isomers of 2 are produced in refluxing pyridine and with maleic anhydride in refluxing toluene. The former is the result of a 1,4-H shift of the CH₂ group γ to the palladium atom on the butadienyl chain whereas the latter is obtained via a 1,5-H shift of the CH₂ unit δ to the palladium.

Introduction

The synthesis of butadienyl fragments η³-bound to a palladium center may be achieved via insertion of two alkynes into Pd–X bonds[1] (X = Cl, Ph) or into the Pd–C bond of cyclopalladated compounds. Several structure determinations[2-5] have shown that the butadienyl units formed invariably display the same features. Each contains one C–C double bond η²-bound at the palladium atom and a second η¹-bound olefin moiety. This bonding

mode is obviously reminiscent of that of allylic fragments. However, in contrast to allylic units whose chemistry has been extensively investigated and which are still part of

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† Reactivity of cyclopalladated compounds part 27. For part 26, see ref 8.