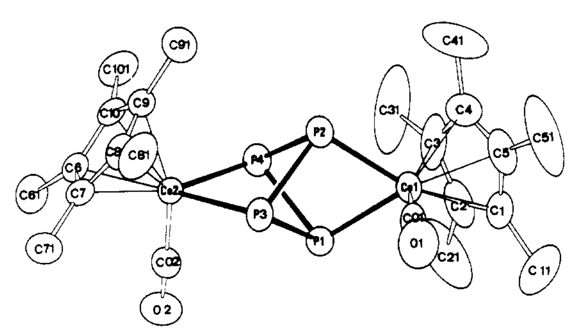

**Figure 2.** ORTEP drawing of complex **3** (50% probability ellipsoids are shown). Selected bond distances (Å) and bond angles (deg): Co1–P1 = 2.256 (2), Co1–P2 = 2.262 (2), Co2–P3 = 2.254 (2), Co2–P4 = 2.254 (2), P1···P2 = 2.560 (2), P3···P4 = 2.597 (2), P1–P3 = 2.221 (2), P2–P3 = 2.234 (2), P1–P4 = 2.227 (2), P2–P4 = 2.236 (2), Co1–Cp*(centr) = 1.738, Co2–Cp*(centr) = 1.737; P1–Co1–P2 = 69.0 (1), P3–Co2–P4 = 70.4 (1), P3–P1–P4 = 71.4 (1), P3–P2–P4 = 71.0 (1), P1–P3–P2 = 70.1 (1), P1–P4–P2 = 70.0 (1), Co1–P1–P3 = 97.9 (1), Co1–P1–P4 = 99.7 (1), Co1–P2–P3 = 97.3 (1), Co1–P2–P4 = 99.3 (1), Co2–P3–P1 = 96.9 (1), Co2–P3–P2 = 98.7 (1), Co2–P4–P1 = 96.7 (1), Co2–P4–P2 = 98.7 (1), P1P3P4|P2P3P4 = 89.8, P1P3P2|P1P4P2 = 90.6°.

**5** (71.1° (average)) are nearly the same as in **2** (70.5°) and **3** (69.0|70.4°). The same holds for the Co–P distances ($\bar{d}$(Co-P) = 2.22|2.26 Å in **5**[8] and 2.26 Å in **2** and **3**). (ii) The $^{31}P\{^1H\}$NMR data[9] of **2** show a much stronger chemical shift difference (Δ = ca. 120 ppm) for the $A_2XY$ system with respect to $\eta^2$-coordinated $P_4$ in **4** ($A_2B_2$ part, $\delta$ = −279.4|−284.0 ppm, Δ = ca. 5 ppm[7]). As with **4**[7] (2.188 (2) Å) the shortest P–P distance in **2** (P3–P4 = 2.158 (2) Å, Figure 1) is opposite to the longest one (P1···P2). The distance in **2** is comparable with that of the phosphabicyclobutane derivatives $P_2(PR)_2$ (**6**) (**6a**,[10a] R = $N(SiMe_3)_2$, 2.129 Å; **6b**,[10b] R = $(tBu)_3C_6H_2$, 2.166 (2) Å; **6c**,[10c] $P_2(PR)(CR'_2)$, R = $(tBu)_3C_6H_2$, R′ = $SiMe_3$, 2.136 (1) Å) and $P_2(CR)_2ZrCp_2$ (**7**)[11] (R = tBu, 2.147 (1) Å). The folding angle between the two $P_3$ "wings" of the "butterfly" is 95° in **2**, 95.2° in **6a**,[10a] 95.5° in **6b**,[10b] 105° in **6c**[10c] ($P_3|P_2C$ "wings") and 110° in **7**[11] (two $P_2C$ "wings" with a $Cp_2Zr$ bridge). In both complexes the planes $P_2Co$|Cp*(centr.)-CoC(O) are approximately orthogonally oriented to each other [**2**, 88.7°; **3**, 88.8 (Co1), 87.4° (Co2)].

The P atoms of the formal $P_4^{4-}$ ligand in **3** form a bent four-membered ring with $\bar{d}$(P–P) = 2.23 Å while the corresponding $\bar{d}$(P–P) is 2.21 Å for the formal $P_4^{2-}$ ligand in **2**. In the solid-state chemistry of polyphosphides[12] a rectangular formal $P_4^{4-}$ was found in $CoP_3$[13] with $\bar{d}$(Co–P) = 2.22 Å and $d$(P–P) = 2.24|2.34 Å.

The $P_4$ unit of **3** completes the series of $P_4^{n-}$ ligands ($n$ = 2, this work and $Cp'_2MP_4$ (M = Zr, Hf, Cp′ = $\eta^5$-1,3-$C_5H_3(tBu)_2$);[6] $n$ = 4, this work and $n$ = 6, $Cp^*_3Ni_3P_5$[14]) in organometallic chemistry.

**Acknowledgment.** We thank the Fonds der Chemischen Industrie for financial support.

**Supplementary Material Available:** Tables of bond distances and angles, crystal data, non-hydrogen atom coordinates, thermal parameters, and hydrogen atom coordinates for **2** and **3** (13 pages); listings of structure factor amplitudes for **2** and **3** (22 pages). Ordering information is given on any current masthead page.

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(9) $^{31}P\{^1H\}$ NMR (80.82 MHz, toluene-$d_8$, 85% $H_3PO_4$ external standard): **2**, $A_2XY$ system, $\delta(P_A)$ = −258.2 (t), $\delta(P_X)$ = −335.9 (q), $\delta(P_Y)$ = −376.9 (q), $^1J$(P–P) = 156 Hz; **3**, AA′XX′ system, $\delta(P_{AA'})$ = −125.1, $\delta(P_{XX'})$ = −165.4, $^1J(P_A–P_X)$ = $^1J(P_A–P_{X'})$ = ±97 Hz, $^1J(P_A–P_{A'})$ = ±56 Hz, $^1J(P_X–P_{X'})$ = ±28 Hz, $^2J(P_A–P_{X'})$ = ±44 Hz. $^1H$ NMR (200 MHz, $C_6D_6$, TMS internal standard): **2**, $\delta$ = 1.31 (s, $CH_3$); **3**, $\delta$ = 1.55 (s, $CH_3$). IR (pentane, $\nu_{CO}$): **2**, 2000 (vs) $cm^{-1}$; **3**, 1990 (vs) $cm^{-1}$.

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## Reactivity of $Ph_2PC{\equiv}CCMe_3$ toward $[PPh_4][HFe_3(CO)_{11}]$: Synthesis and X-ray Structure of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH(CMe_3))]$ and $[PPh_4][Fe_2(CO)_6(\mu\text{-}PPh_2CH{=}C(CMe_3)C(O))]\cdot CH_2Cl_2$

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*Received October 17, 1988*

*Summary:* The reaction of $Ph_2PC{\equiv}CCM_3$ with $[PPh_4][HFe_3(CO)_{11}]$ in boiling ethyl acetate leads to the formation of $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH(CMe_3))]$ as the main product in which phosphorus–alkynyl bond cleavage has occurred and migration of hydrogen onto the $\beta$-carbon has led to a vinylidene ligand. The second product, $[PPh_4][Fe_2(CO)_6(\mu\text{-}Ph_2PCH{=}C(CMe_3)C(O))]$, contains a bridging ligand that results from hydrogen migration on the $\alpha$-carbon of the alkynyl group and CO insertion between the $\beta$-carbon and one iron atom.

The reactivity of (diphenylphosphino)alkynes, $Ph_2PC{\equiv}CR$, toward polynuclear complexes has been extensively investigated by Carty et al.[1] during the last decade and has led to interesting rearrangement reactions implying generally the breaking of the phosphorus–alkynyl bond.[1,2] Considering the great reactivity of $[PPh_4][HFe_3(CO)_{11}]$ (**1**), toward alkynes which we have recently pointed out,[3] we thought it of interest to check the behavior of these ligands toward this cluster anion. Indeed, in this case, the presence of an hydrido ligand could extend the type of reactivity observed by the possible insertion of the carbon–carbon triple bond into the iron–hydrogen

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[†] Unité No. 8241 liée par conventions á l'Université Paul Sabatier et á l'Institut National Polytechnique.

(1) Nucciarone, D.; McLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 106–177 and references therein.

(2) See for instance: Van Gastel, F.; McLaughlin, S. A.; Lynch, M.; Carty, A. J.; Sappa, E.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Organomet. Chem.* **1987**, *326*, C65–C70.

(3) (a) Lourdichi, M.; Mathieu, R. *Nouv. J. Chim.* **1982**, *6*, 231–233. (b) Suades, J.; Mathieu, R. *J. Organomet. Chem.* **1986**, *312*, 335–341. (c) Lourdichi, M.; Mathieu, R. *Organometallics* **1986**, *5*, 2067–2071.

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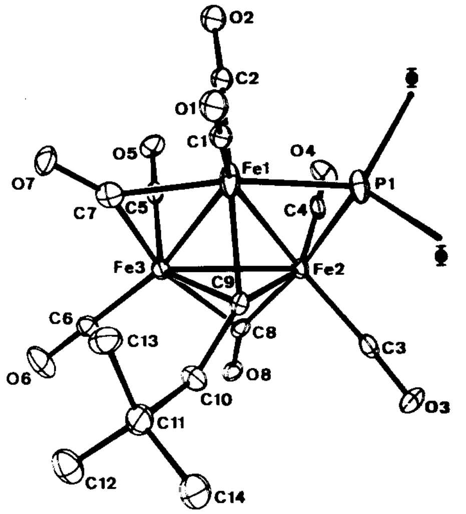

**Figure 1.** ORTEP view of the anionic part of 2 showing the atomic numbering scheme. The phenyl groups and hydrogen atom have been omitted for the sake of clarity and only one of the two positions of the disordered C(1)–O(1) and C(2)–O(2) groups has been represented. Selected bond distances (Å) and angles (deg): Fe(1)–Fe(2) = 2.5784 (7), Fe(2)–Fe(3) = 2.5004 (7), Fe(3)–Fe(1) = 2.4803 (7), Fe(1)–P(1) = 2.179 (1), Fe(2)–P(1) = 2.219 (1), Fe(1)–C(9) =1.913 (4), Fe(2)–C(9) = 1.955(4), Fe(3)–C(9) = 2.013 (3), Fe(3)–C(10) = 2.292 (4), C(9)–C(10) = 1.378 (5), C(10)–C(11) = 1.539 (5), Fe(1)–C(7) = 2.062 (4), Fe(3)–C(7) = 1.902 (4), Fe(2)–C(8) = 1.862 (4), Fe(3)–C(8) = 2.175 (4); Fe(3)–Fe(1)–Fe(2) = 59.21 (2), Fe(1)–Fe(2)–Fe(3) = 58.44 (2), Fe(2)–Fe(3)–Fe(1) = 62.35 (2), Fe(1)–P(1)–Fe(2) = 71.78 (3), Fe(1)–Fe(2)–P(1) = 53.38 (3), Fe(2)–Fe(1)–P(1) = 54.84 (3), Fe(1)–C(9)–C(10) = 139.7 (3), C(9)–C(10)–C(11) = 128.3 (3), C(9)–C(10)–H(C10) = 116.0, Fe(1)–C(7)–O(7) = 137.1 (3), Fe(3)–C(7)–O(7) = 145.0 (3), Fe(2)–C(8)–O(8) = 152.5 (3), Fe(3)–C(8)–O(8) = 131.3 (3).

bond. The literature gives one precedent only of this type of reaction with the cluster $HRu_3(CO)_9(\mu\text{-}PPh_2)$.[2]

Actually, we have observed that the reactions are very complex and R-dependent, and we report here the results observed in the case where R = $CMe_3$.

The reaction of 1 with 1 equiv $Ph_2PC{\equiv}CCMe_3$ in boiling ethyl acetate leads to a mixture of two products that are separated by fractional crystallization in dichloromethane/methanol. The main product of the reaction, **2**, is a dark green solid that has been fully characterized by multinuclear NMR, IR,[4] and single-crystal X-ray diffraction.

The most infomative spectra data are provided by $^{31}P$ and $^{1}H$ NMR spectra. The $^{31}P$ NMR spectrum shows a resonance at 273.9 ppm, suggesting the presence of a phosphido group bridging an Fe–Fe bond[5] while the $^{1}H$ NMR spectrum gives evidence of a CH group that appears as a doublet centered at 5.02 ppm ($J_{PH}$ = 12 Hz).

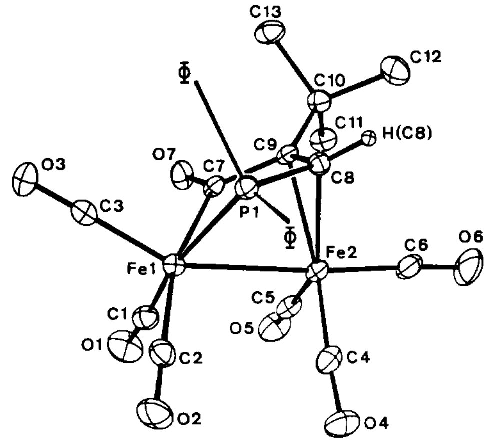

**Figure 2.** ORTEP view of the anionic part of 3 showing the atomic numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)–Fe(2) = 2.6795 (7), Fe(1)–P(1) = 2.212 (1), Fe(1)–C(7) = 2.067 (3), Fe(2)–C(8) = 2.068 (4), Fe(2)–C(9) = 2.085 (3), P(1)–C(8) = 1.754 (3), C(8)–C(9) = 1.420 (5), C(9)–C(10) = 1.545 (5), C(9)–C(7) = 1.473 (5), C(7)–O(7) = 1.230 (5); Fe(1)–P(1)–C(8) = 98.1 (1), P(1)–C(8)–C(9) = 114.2 (3), P(1)–C(8)–H(C8) = 114 (2), C(8)–C(9)–C(7) = 115.0 (3), C(8)–C(9)–C(10) = 122.9 (3), C(9)–C(7)–Fe(1) = 114.4 (2), C(9)–C(7)–O(7) = 123.4 (3), Fe(1)–C(7)–O(7) = 122.0 (3).

The precise nature of 2 has been established by X-ray diffraction,[6] and the structure of its anionic part is shown in Figure 1. It consists of a triangle of iron atoms, with Fe(1)–Fe(2) bridged by a diphenylphosphido bridge lying approximately in the triangle plane while the other two sides are bridged by a carbonyl group. A $C{=}CHCMe_3$ vinylidene group is $\sigma$-bonded to Fe(1) and Fe(2) and $\pi$-bonded to Fe(3). Each iron atom is bonded to two terminal carbonyl groups. This structure closely resembles that of $Ru_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CR)$ complexes that result from the reaction of the phosphinoalkynes with $Ru_3(CO)_{12}$.[1]

Upon formation of 2, phosphorus–alkynyl bond breaking has occurred and the hydride ligand has migrated onto the $\beta$-carbon, generating the vinylidene ligand.

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(4) $[PPh_4][HFe_3(CO)_{11}]$ (1 g) and $Ph_2PC{\equiv}CCMe_3$ (0.35 g) were refluxed for 2 h in 25 mL of ethyl acetate. Evaporation of the solvent and crystallization in $MeOH/CH_2Cl_2$ afforded **2** (0.7 g, 55% yield): IR ($CH_2Cl_2$) $\nu$(CO) 2010 (s), 1960 (vs), 1930 (s), 1810 (sh), 1785 (m) $cm^{-1}$; $^{1}H$ NMR ($(CD_3)_2CO$) 8.04 (m, $PPh_4^+$), 4.98 (d, $J_{PH}$ = 4.4 Hz, H), 0.99 (s, $CMe_3$) ppm; $^{31}P$ NMR ($(CD_3)_2CO$) 273.9 ($PPh_2$), 28.4 ($PPh_4^+$) ppm; $^{13}C$ NMR ($CD_2Cl_2$) except phenyl resonances, 232.6 (d, $J_{PC}$ = 57 Hz, $CCHCMe_3$), 227.3 (br, CO), 37.0 ($CMe_3$), 31.2 ($CMe_3$) ppm. Anal. Calcd for $C_{50}H_{40}Fe_3O_8P_2$: C, 60.12; H, 4.01. Found: C, 59.95; H, 4.12. Evaporation of the mother solution and crystallization in $CH_2Cl_2/(i\text{-}Pr)_2O$ afforded **3** (0.2 g, 20% yield): IR ($CH_2Cl_2$) $\nu$(CO) 2015 (s), 1955 (vs), 1945 (sh), 1925 (s), 1895 (m), 1615 (m) $cm^{-1}$; $^{1}H$ NMR ($(CD_3)_2CO$) 8.04 (m, $PPh_4^+$), 3.64 (d, $J_{PH}$ = 0.3 Hz, H), 1.28 (s, $CMe_3$) ppm; $^{31}P$ NMR ($(CD_3)_2CO$) 57.5 ($PPh_2$), 28.4 ($PPh_4^+$) ppm; $^{13}C$ NMR ($CD_2Cl_2$) except phenyl resonances, 230.5 (C=O), 219.4 (C≡O), 90.4 ($CCMe_3$), 35.6 (dd, $J_{CH}$= 161.8 Hz, $J_{PC}$ = 37 Hz), 34.7 ($CMe_3$), 29.7 (q, $J_{CH}$ = 127 Hz, $CMe_3$) ppm.

(5) McLaughlin, S. A.; Nucciarone, D.; Carty, A. J. *Phosphorus 31 NMR Spectroscopy in Stereochemical Analysis, Organic Compounds, and Metal Complexes*; Verkade J. G., Quinn, L. D., Eds.; VCH Publishers: New York, 1987; Chapter 16.

(6) Crystal data for $C_{50}H_{40}O_8P_2Fe_3$: $M_r$ 998.4; triclinic; $a$ = 14.881 (3) Å, $b$ = 16.169 (4) Å, $c$ = 9.424 (2) Å, $\alpha$ = 91.12 (2)°, $\beta$ = 91.90 (2)°, $\gamma$ = 93.10 (2)°, $V$ = 2262 (2) $Å^3$ (by least-squares refinement on a CAD 4 diffractometer for 25 automatically centered reflections, $\lambda$ = 0.710 73 Å); space group $P\bar{1}$; $Z$ = 2; $D_{calcd}$ = 1.466 $g{\cdot}cm^{-3}$; green dark parallelepipedic crystal (0.30 × 0.25 × 0.45 mm) sealed on a glass fiber; $\mu$(Mo K$\alpha$) = 10.7 $cm^{-1}$; $T$ = 103 K (low device temperature: Bonnet, J.-J.; Askenazy, S., commercially available as NJET from Soterem, ZI de Vic, 31320 Castanet Tolosan, France). **Data collection and processing**: Intensity data were recorded by the $\omega/2\theta$ scan technique (scan width = 1.00° + 0.35° tan $\theta$; scan speed = 2.1 $deg{\cdot}min^{-1}$). A set of 4840 independent reflections was collected ($1.0 < \theta < 21°$; $\pm h,\pm k,l$) and corrected for Lorentz and polarization effects (Frentz, B. A. *SDP, Structure Determination Package*; Enraf Nonius: Delft, Holland, 1982). Standard intensity reflections, recorded periodically, showed only random statistical fluctuations. A total of 4051 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. No absorptions corrections were made. **Structure determination**: Structure was solved by direct method techniques (Sheldrick, G. M. *SHELXS 86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, FRG, 1986) and refined by full-matrix least-squares refinement (Sheldrick, G. M. *SHELX 76, Program for Crystal Structure Solution*; University of Cambridge: Cambridge, England, 1976). All atoms were located. Two carbonyls, viz. C(1)–O(1) and C(2)–O(2), appeared to be disordered. Their respective two positions were refined isotropically with an occupancy factor of 0.5. Phenyl rings were refined as isotropic rigid groups (C–C = 1.395 Å). Hydrogen atoms were introduced in calculations in constrained geometry (C–H = 0.95 Å). All other atoms were refined anisotropically. Neutral scattering factors were used, those for non-hydrogen atoms being corrected for anomalous dispersion, $f'$, $f''$ (*International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2.B, p 99; Table 2.3.1, p 149; Table 2.2.C, p 102). The final full-matrix least-squares refinement converged to $R$ = 0.027 and $R_w$ = 0.029 with unit weights. The error in an observation of the unit weight was $S$ = 1.26 with 4051 observations and 312 variables. A final difference Fourier map showed a residual electron density of 0.5 $e/Å^3$.

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This situation has to be contrasted to the result obtained during the reaction of phosphinoalkynes with $HRu_3(CO)_9(\mu\text{-}PPh_2)$, which shows that in this case hydride migration has occurred onto the $C_\alpha$ carbon, generating a primary alkyne subsequent to phosphorus bond breaking.[2]

The second product of the reaction, **3**, is an orange solid that presents very different spectroscopic properties compared to those of **2**. More specifically, the $^{31}P$ NMR spectrum shows a resonance at 57.5 ppm while a CH group is observed in the proton NMR spectrum at 3.64 ppm with a small coupling of 0.3 Hz with phosphorus. Moreover, the $^{13}C$ NMR spectrum confirms the presence of a CH group as a double doublet centered at 34.9 ppm ($J_{CH}$ = 161.8 Hz, $J_{PC}$ = 37 Hz), and, except for CO, Ph, and $CMe_3$ resonances, two signals are observed at 90.4 and 230.5 ppm.

The nature of **3** has been established by X-ray structure determination,[7] and the structure of the anionic part of **3** is shown in Figure 2. **3** is a dinuclear complex containing two $Fe(CO)_3$ units at bonding distances. This dinuclear unit is bridged by a five-electron organic ligand resulting from hydride migration onto the α–carbon of the alkynyl group and coupling of the β-carbon with carbon monoxide. This ligand is π-bonded to Fe(1) through phosphorus and through the carbon of the ketonic group and π-bonded to Fe(2) through the C(8)–C(9) double bond.

We may attribute the $^{13}C$ NMR resonances observed at 90.4 and 230.5 ppm to C(9) and C(7), respectively. Thus, the formation of **3** implies cluster fragmentation into a dinuclear species, migration of the hydride ligand onto the α-carbon of the alkynyl group, and insertion of a CO group between the β-carbon and Fe(1). The latter reaction has been precedented during acetylene–acetylide coupling via reactions of $Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}C{\equiv}CR)$ complexes with alkynes.[8]

To conclude, the reaction of $Ph_2PC{\equiv}CCMe_3$ with $[PPh_4][HFe_3(CO)_{11}]$ in boiling ethyl acetate has led to the formation of two products. The main product, **2**, results from the cleavage of the phosphorus–alkynyl bond and subsequent migration of the hydride ligand onto the β-carbon, generating $PPh_2$ and $C{=}CH(CMe_3)$ bridging ligands. In the second product, **3**, cluster fragmentation into a dinuclear complex bridged by the $Ph_2PC(H){=}C(CMe_3)C(O)$ ligand is observed. This result illustrates further the great versatility of (diphenylphosphino)alkynes toward cluster complexes.

**Acknowledgment.** J.S. thanks the CICYT for a grant (No. PB86-0274).

**Supplementary Material Available:** Tables of final atomic coordinates, final anisotropic thermal parameters, and bond lengths and angles for $[PPh_4][Fe_3(CO)_6(\mu\text{-}CO)_2(\mu\text{-}PPh_2)(\mu\text{-}C{=}CH(CMe_3))]$ and for $[PPh_4][Fe_2(CO)_6(\mu\text{-}Ph_2PCH{=}C(CMe_3)C(O))]$ (12 pages); listings of structure factor amplitudes (40 pages). Ordering information is given on any current masthead page.

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[7] Crystal data for $C_{49}H_{40}O_7P_2Fe_2{\cdot}CH_2Cl_2$; $M_r$ 999.4; triclinic; $a$ = 15.096 (2) Å, $b$ = 16.332 (2) Å, $c$ = 9.683 (1) Å, $\alpha$ = 92.60 (1)°, $\beta$ = 95.21 (1)°, $\gamma$ = 78.64 (1)°, $V$ = 2330.0 (8) Å$^3$ (obtained as for ref 6); space group $P\bar{1}$; $Z$ = 2; $D_{calcd}$ = 1.424 g·cm$^{-3}$; orange plate crystal (0.50 × 0.50 × 0.075 mm) sealed on a glass fiber; $\mu$(Mo K$\alpha$) = 8.5 cm$^{-1}$; $T$ = 293 K. **Data collection and processing**: intensity data were recorded by the $\theta/2\theta$ scan technique (scan width = 0.95° + 0.35° tan $\theta$; scan speed = 1.0–6.9 deg·min$^{-1}$). A set of 5827 independent reflections was collected ($1.5 < \theta < 22.5°$; $\pm h,\pm k,l$) and corrected for Lorentz and polarization effects (see ref 6). Standard intensity reflections, recorded every 2 h, showed no significant fluctuations. Empirical absorptions corrections (North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351–359) were applied: $T_{min}$ = 0.82; $T_{max}$ = 1.00. A total of 4186 reflections with $I > 3\sigma(I)$ were used in structure solution and refinement. **Structure determination**: Structure was solved and refined as in ref 6. All non-hydrogen atoms were refined anisotropically but phenyl rings which were refined as isotropic rigid groups (C–C = 1.395 Å). Hydrogen atoms were located on a difference Fourier map at their expected positions and introduced in calculations in constrained geometry (C–H = 0.97 Å) except that bonded to C(8), which was allowed to vary. Scattering factors were those of ref 6. The final full-matrix least-squares refinement converged to $R$ = 0.032 and $R_w$ = 0.032 with unit weights. $S$ had the value 1.1 with 4186 observations and 319 variables. A final difference Fourier map showed a residual electron density of 0.3 e/Å$^3$.

[8] Smith, W. F.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1976**, *896*–898.

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# Reaction between Transition-Metal Nucleophiles and Alkanedioyl Dichlorides: Preparation of Five- and Six-Membered Metal-Substituted Lactone Complexes $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}\overline{C{:}CH(CH_2)_nC(O)O}$ (M = Mo, W; $n$ = 1, 2)

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*Summary:* Unsaturated, unconjugated five- and six-membered transition-metal-substituted lactone complexes $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}\overline{C{:}CH(CH_2)_nC(O)O}$ (M = Mo, W; $n$ = 1, 2) are prepared by reacting $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ with succinyl and glutaryl dichlorides. The reaction mechanism involves the formation of a monometallic alkanedioyl chloride complex, followed by a base-assisted cyclization reaction.

The reaction of transition-metal nucleophiles with α,ω-dihaloalkanes is known to produce dimetalloalkanes,[1] monosubstituted alkyl halides,[2] or oxacycloalkylidenes,[3] depending on the metals and halides involved. In contrast, the reaction between transition-metal nucleophiles and α,ω-alkanedioyl dihalides only produce dimetallic alkanedioyl complexes.[2,4] For example, King, Petit, and their co-workers prepared several $FpC(O)\text{–}(CH_2)_n\text{–}(O)CFp$ (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$, $n$ = 2–4) by reacting the strongly nucleophilic $Fp^-$ with the corresponding alkanedioyl dichlorides, presumably via a disubstitution mechanism.[2,4a] We were attempting to prepare heterobimetallic bridging bis(acyl) complexes by successive acylations of bis(acyl) dichloride with two different metal anions. Herein we wish to describe some unexpected results we obtained from the reaction of $Na[(\eta^5\text{-}C_5H_5)M(CO)_3]$ (M = Mo, **1a**; M = W, **1b**) with succinyl and glutaryl dichlorides. Instead of the expected bimetallic products, we isolated novel unsaturated and unconjugated five- and six-membered metal-substituted lactones $(\eta^5\text{-}C_5H_5)(CO)_3M\text{–}\overline{C{:}CH(CH_2)_nC(O)O}$ (M = Mo, $n$ = 1, **2a**; M = W, $n$ = 1, **2b**; M = Mo, $n$ = 2, **3a**; M = W, $n$ = 2, **3b**) under a variety of conditions.

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