

## The Extremely Rapid Acid-catalysed Isomerizations of Carbonyl-Mo or -W Tertiary Phosphine Complexes: Convenient Syntheses of *fac*- or *mer*-Isomers

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Acid, at a concentration frequently present in solvents such as dichloromethane, causes rapid interconversion of *fac*- and *mer*-[W(CO)<sub>3</sub>(dppm-PP')L] (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>, L = PEt<sub>3</sub> or PEt<sub>2</sub>Ph) via a 7-co-ordinate hydride intermediate, [WH(CO)<sub>3</sub>(dppm-PP')L]<sup>+</sup>: convenient syntheses are developed, based on these protonation reactions, including the conversion of *fac*-[Mo(CO)<sub>3</sub>(dppm-PP')(dppm-P)] into the more useful *mer*-isomer.

Many tertiary phosphine-Group VI metal carbonyl complexes of the types [M(CO)<sub>x</sub>L<sub>y</sub>](M = Cr, Mo, or W; x = 1-4; L = PR<sub>3</sub> or L-L = a diphosphine), have been made and their physical and chemical properties studied very extensively.<sup>1</sup> We now report an acid-catalysed isomerization of *fac*- and *mer*-phosphine-substituted tricarbonyls of Mo or W which is so fast that the trace amount of acid, normally present in solvents such as dichloromethane, is sufficient to cause equilibration *fac* ⇌ *mer* in a few minutes at 20°C. Dichloromethane has frequently been used as a solvent in this sort of chemistry, for example in i.r. and n.m.r. spectroscopic studies, in electrochemistry, and in other chemical reactions.<sup>1-4</sup>

Treatment of [W(CO)<sub>4</sub>(dppm-PP')] (dppm = Ph<sub>2</sub>PCH<sub>2</sub>-PPh<sub>2</sub>) with PEt<sub>3</sub> in boiling n-decane for 6 h gave a mixture of *fac*- and *mer*-[W(CO)<sub>3</sub>(PEt<sub>3</sub>)(dppm-PP')], from which only the *fac*-isomer crystallized out at 0°C, albeit in poor yield (ca. 20%). We were unable to isolate the pure *mer*-isomer from the mixture by fractional crystallization. The <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum† of the *fac*-isomer consists of a 1:1 doublet {δ<sub>P</sub>

(dppm) -24 p.p.m.} and a 1:2:1 triplet {δ<sub>P</sub> (PEt<sub>3</sub>) -3.1 p.p.m., J(PP) 24 Hz} each with satellites due to coupling to <sup>183</sup>W (I = 1/2, 14% abundant), J(WP) = 215 Hz, in each case. A solution of this *fac*-isomer in acid-free dichloromethane-CDCl<sub>3</sub> remained unchanged over several hours at 20°C. However, commercial dichloromethane frequently contains acid (typically 5 × 10<sup>-4</sup> M HCl) and we found that in such unpurified dichloromethane or in purified (acid free) dichloromethane to which a little acid had been added, e.g. CF<sub>3</sub>CO<sub>2</sub>H or HBF<sub>4</sub>·Et<sub>2</sub>O (ca. 10<sup>-3</sup> M), an equilibrium *fac* ⇌ *mer*, with approximately equal amounts of each, was established in a few minutes at 20°C, as evidenced by the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum (see below for <sup>31</sup>P-{<sup>1</sup>H} n.m.r. data for the *mer*-isomer). It seemed likely that the rapid equilibration *fac* ⇌ *mer* involved a fluxional 7-co-ordinate hydride intermediate, [WH(CO)<sub>3</sub>(PEt<sub>3</sub>)(dppm-PP')]<sup>+</sup> and, indeed, when we treated a 1.8 × 10<sup>-2</sup> M solution of [W(CO)<sub>3</sub>(PEt<sub>3</sub>)(dppm-PP')] with a small excess of CF<sub>3</sub>CO<sub>2</sub>H (5% excess), conversion into the protonated species, [WH(CO)<sub>3</sub>(PEt<sub>3</sub>)(dppm-PP')]<sup>+</sup>, was complete, as evidenced by the <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectrum at -50°C {δ(P<sub>A</sub>) 10.2 p.p.m., δ(P<sub>B</sub>) -27.5 p.p.m., δ(P<sub>C</sub>) -40.9 p.p.m., J(P<sub>A</sub>P<sub>B</sub>) 7, J(P<sub>A</sub>P<sub>C</sub>) 10, J(P<sub>B</sub>P<sub>C</sub>) 66 Hz, J(WP) 148 (P<sub>A</sub>), 156 (P<sub>B</sub>), and 151 Hz (P<sub>C</sub>); the designations P<sub>A</sub>, P<sub>B</sub>, and P<sub>C</sub> are arbitrary} and also the <sup>1</sup>H and <sup>1</sup>H-{<sup>31</sup>P} n.m.r. spectra

† This and other <sup>31</sup>P-{<sup>1</sup>H} n.m.r. spectra were recorded in CH<sub>2</sub>Cl<sub>2</sub>-CDCl<sub>3</sub> (3:1 v/v).

(at  $-50^{\circ}\text{C}$ ), which showed a hydride resonance at  $\delta -1.58$  p.p.m. coupled approximately equally to two P-nuclei ( $J$  56 Hz). This hydride species showed i.r. bands at 2042m, 1980m, and 1924s  $\text{cm}^{-1}$ , compared with  $\nu(\text{C}=\text{O})$  bands for  $[\text{W}(\text{CO})_3(\text{PEt}_3)(\text{dppm-PP}')] ]$ : *fac* 1932vs and 1830vs  $\text{cm}^{-1}$ ; and *mer*: 1954m, 1852vs, and 1832sh  $\text{cm}^{-1}$  (both determined in acid-free dichloromethane solution). The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of the protonated species showed that the three P-nuclei were no longer equivalent, *i.e.* a similar arrangement to that in *mer*- $[\text{W}(\text{CO})_3(\text{PEt}_3)(\text{dppm-PP}')] ]$ , and when we treated a dichloromethane solution of the *fac*-isomer with a 10% excess of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ , followed, after 2 minutes, by an excess of triethylamine, conversion to the *mer*-isomer appeared to be quantitative [ $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. evidence] and the pure *mer*-isomer was readily isolated (80% yield). The  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum of the *mer*-isomer, in acid-free  $\text{CD}_2\text{Cl}_2$ , showed  $\delta(\text{P}_A)$  9.3 p.p.m.,  $\delta(\text{P}_B) - 24.0$  p.p.m.,  $\delta(\text{P}_C) - 12.7$  p.p.m.,  $J(\text{P}_A\text{P}_B)$  24,  $J(\text{P}_A\text{P}_C)$  61,  $J(\text{P}_B\text{P}_C)$  29 Hz,  $J(\text{WP})$  280 ( $\text{P}_A$ ), 251 ( $\text{P}_B$ ), and 188 ( $\text{P}_C$ ) Hz. Acid catalysis was also used to convert the *mer*- to the *fac*-isomer in high yield. A near saturated solution of the *mer*-isomer in dichloromethane was treated with  $\text{CF}_3\text{CO}_2\text{H}$  (5 mol %) and the resultant solution was then cooled to  $0^{\circ}\text{C}$ ; the pure *fac*-isomer crystallized out in 84% yield. We have also shown that treatment of a solution of the *mer*-isomer with a catalytic amount of acid gave a *fac/mer* equilibrium with a virtually identical  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum to that obtained by treatment of the *fac*-isomer with a trace of acid. Treatment of the *mer*-isomer with an excess (10%) of  $\text{CF}_3\text{CO}_2\text{H}$  gave the same protonated complex as was obtained from the *fac*-isomer, as evidence by the  $^{31}\text{P}\{-^1\text{H}\}$  n.m.r. spectrum. Thus it is possible to interconvert the *fac*- and the *mer*-isomers very conveniently and in high yield *via* the protonated species; novel methods of syntheses which could probably be extended to many other systems. We have similarly made and interconverted *fac*- and *mer*- $[\text{W}(\text{CO})_3(\text{PEt}_2\text{Ph})(\text{dppm-PP}')] ]$ .

These results suggested that acid catalysis might be conve-

niently used to convert *fac*- $[\text{Mo}(\text{CO})_3(\text{dppm-PP}')](\text{dppm-P})$  into the more useful *mer*-isomer, which readily ring-opens on treatment with a variety of metal complexes, to give heterobimetallics containing the moiety  $\text{M}(\mu\text{-dppm})_2\text{M}'$ ,  $\text{M} = \text{Mo}$ ;  $\text{M}' = \text{Cu, Ag, Au, Pd, Pt, Rh, or Ir}$ .<sup>5</sup> *fac*- $[\text{Mo}(\text{CO})_3(\text{dppm-PP}')](\text{dppm-P})$  is readily prepared by treating  $[\text{Mo}(\text{CO})_3(\text{cycloheptatriene})]$  with *dppm* in dichloromethane<sup>3</sup> and we now find that treatment of its solution in dichloromethane with a slight excess of  $\text{HBF}_4\cdot\text{Et}_2\text{O}$ , followed by triethylamine, gives the corresponding *mer*-isomer in essentially quantitative yield. Our results suggest an explanation for a report that treatment of  $[\text{Mo}(\text{CO})_3(\text{cycloheptatriene})]$  with *dppm* in benzene gives *mer*- $[\text{Mo}(\text{CO})_3(\text{dppm-PP}')](\text{dppm-P})$ .<sup>3</sup> We have found that, in contrast, this treatment gives only the *fac*-isomer and we suggest that the reaction system used previously<sup>3</sup> contained acid, or a proton source. Although our examples of very rapid acid catalysis have thus far been with *fac*- and *mer*-isomers it seems likely that many other systems will show the phenomenon and that great care should be exercised in freeing solvents from acids or sources of protons.

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