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Preliminary communication

Detection of the motions of ancillary bridging ligands during carbon monoxide replacement by trimethylphosphite

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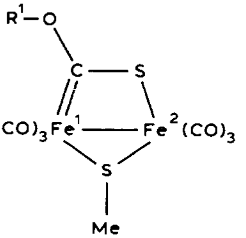
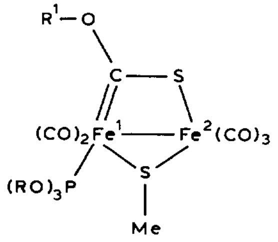
Abstract

A hidden process involving the rotation of a two atom bridge (>C–S–) over a Fe–Fe bond has been revealed by studying the replacement of two carbon monoxide ligands by the sequential use of $P(OCH_3)_3$ and $P(OCD_3)_3$ in a dinuclear dissymmetrical diiron compound.

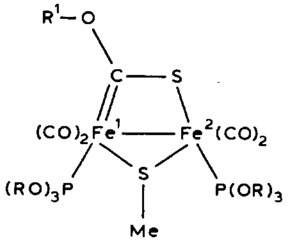
Numerous papers [1–3] devoted to ligand exchange provide evidence of the importance of this reaction in connection with homogeneous and heterogeneous catalysis. When the overall reaction involves a simple replacement of a neutral two electron ligand by a more basic one, the participation of ancillary ligands during the stereochemical course of the reaction is not always detectable. Partial and temporary decoordination of polyhapto ligands may be demonstrated by kinetic mea-



(1)



(2 : R = CH_3;
4 : R = CD_3)



(3 : R = CH_3;
5 : R = CD_3)

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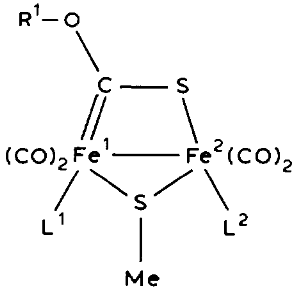
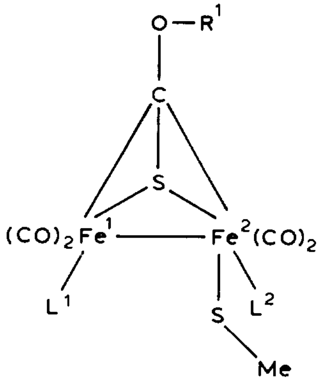


$(6: L^1 = P(OCH_3)_3;\ L^2 = P(OCD_3)_3;$

$7: L^1 = P(OCD_3)_3;\ L^2 = P(OCH_3)_3)$



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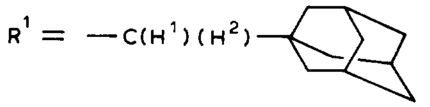

surements for associative substitution reactions at 18-electron centers [3], but examples involving bridging or capping ligands in polynuclear compounds are scarce, and demonstration of their occurrence requires the use of multiple stereochemical or spectroscopic probes [4–7]. We report here an example of a hidden process occurring during the replacement of carbon monoxide in a dissymmetrical diiron compound. This process is revealed by the sequential use of $P(OCH_3)_3$ and its labeled analog $P(OCD_3)_3$ [8 *].

The synthesis and structural determination of the coordination compounds **1**, **2** and **3** have been described [9–11]. The disubstituted complex **3** is obtained in a process which obeys the empirical rule of one carbonyl exchange at each metal center [2], directly from **1** or stepwise via **2** by use of thermal activation or electron transfer catalysis. However when the second substitution was brought about by adding $P(OCD_3)_3$ to a solution of **2**, instead of the expected exclusive formation of compound **6** we obtained a mixture of **5**, **6** and **7**. Similarly when started from the labeled mono-substituted compound **4** the reaction with $P(OCH_3)_3$ gave a mixture of **3**, **6** and **7**. We confirmed that ligand exchange does not occur between **5** and $P(OCH_3)_3$ or between **3** and $P(OCD_3)_3$.

All the structures were established by conventional techniques, and the mixtures **6** + **7** and **3** + **5** were analysed by high field ^1H NMR spectroscopy (Table 1). The chemical shifts are different depending on whether $P(OCH_3)_3$ is linked to Fe^1 or to Fe^2 in complex **3**.

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* A reference number with an asterisk refers to a note in the reference list.

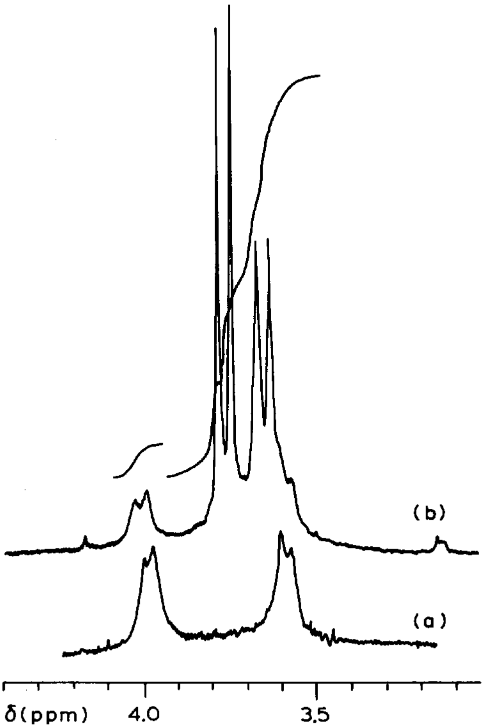

Fig. 1. ^1H NMR Spectra ($CDCl_3$, 36 °C) of disubstituted diiron compounds. (a) Spectrum of **5**. (b) Spectrum of disubstituted compounds formed in the reaction **2** + $P(OCD_3)_3$.

It is noteworthy that the methylene protons of the substituent R^1 are non equivalent (for **5** $\delta(^1H)$ 4.04; $\delta(^2H)$ 3.60 ppm; ^2J (9 Hz). This feature, shown in Fig. 1, is partly masked by the resonance of $P(OCH_3)_3$ in compounds **2**, **3**, **6** and **7** but remains useful for the structural determination.

From the results of Table 1, two main conclusions can be drawn: (i) the formation of **3** or **5** from **4** or **2**, respectively, in the presence of $P(OCH_3)_3$ or

Table 1

$P(OCH_3)_3$ content and repartition in the disubstituted diiron compounds formed by ligand exchange.

Reaction [a]	$P(OCH_3)_3$ [b] content (%)	Repartition of $P(OCH_3)_3$ [c] $(CH_3O)_3P\ Fe^2/Fe^1P(OCH_3)_3$
2 + $P(OCD_3)_3$	28	0.97
4 + $P(OMe)_3$	85	0.94
3 + $P(OCD_3)_3$	95	0.98
5 + $P(OMe)_3$	0	-
2 + $P(OMe)_3$	100	0.97

[a] Monosubstituted compound and excess of $P(OCD_3)_3$ or $P(OMe)_3$ in acetone are heated for 12 h. Mixtures of disubstituted compounds are isolated by thin layer chromatography with 60% yield. [b] $P(OCH_3)_3$ contents are calculated from the integration of trimethylphosphite signals versus integration of protons of R^1 and SMe groups. [c] The repartitions of $P(OCH_3)_3$ on the metal centers are calculated from the integrations in the 3.5–3.7 ppm region ($Fe^2P(OCH_3)_3$ + one methylenic proton) and 3.7–3.9 ppm region ($Fe^1P(OCH_3)_3$) (Fig. 1).

$P(OCD_3)_3$ shows that exchange of phosphite occurs at the metal center Fe^1 already substituted. This reaction leads to a significant deviation of $P(OCH_3)_3$ content from the expected 50%; and (ii) when carbon monoxide replacement occurs at Fe^2, complexes **6** and **7** are obtained in 1/1 ratio. In view of the inability of $P(OR)_3$ ligands to migrate along a metal–metal axis our results imply that the bridging organic ligand $(>C{-}S{-})$ rotates during the overall ligand substitution process.

In a recent paper by Ohst and Kochi [4] emphasis was put on the active role played by the capping ligand in a cluster during electron-transfer catalysis of ligand substitution. Our results demonstrate that ancillary bridging ligands can also be involved in ligand substitutions carried out under thermal activation. The motion of the two atom bridge $(>C{-}S{-})$ can occur via a transient intermediate such as **8** in which the carbon loses its carbenic character to bind the two metal atoms. Because the two metal atoms in **6** and **7** are coordinated to phosphorus ligands of very similar stereoelectronic properties it is not surprising that equal amounts of **6** and **7** are produced in the bonds reorganization. The same conclusion concerning the rotation of the $(>C{-}S{-})$ bridge can also be drawn from other experiments involving alternative use of $P(OCH_3)_3$ and t-BuNC, the results will be reported soon; however, the structural proof in these cases required several X-ray structure determinations. Obviously use of these $P(OCH_3)_3$-$P(OCD_3)_3$ system is faster and easier than the sequential use of other pairs of ligands.

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8 $P(OCH_3)_3$ is the trimethyl phosphite with natural isotopic composition; $P(OCD_3)_3$ was prepared by refluxing $P(NMe_2)_3$ and CD_3OD for 6 h and was purified by distillation. The mass spectrum shows an isotopic purity of 99% and the ^1H NMR spectrum exhibits the multiplets expected for $P(OCD_3)_2(OCD_2H)$.

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