Phosphorus Ligand Migration

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Slow Migration of a Phosphorus Ligand between Two Metal Centers**

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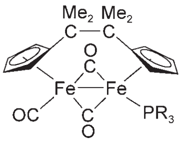
Fluxional behavior is an important phenomenon often observed in many transition-metal complexes by means of dynamic NMR spectroscopy.[1–4] One of the most frequently mentioned textbook examples is the fluxional behavior of the carbonyl ligands in the bis(cyclopentadienyl)diiron complex $[(\eta^5\text{-}C_5H_5)_2Fe_2(\mu\text{-}CO)_2(CO)_2]$ (**1**), which proceeds via interchange of the bridging and terminal CO ligands according to the Adams–Cotton mechanism.[2–6] While many ligands, such as CNR and NO, exhibit similar fluxional behavior, it has long been asserted that phosphorus ligands PR_3 are unable to participate in such fluxional processes.[5] This belief is most clearly illustrated by the dynamic NMR-spectroscopic study of the ring-bridged system $[(\eta^5,\eta^5\text{-}C_5H_4Me_2CCMe_2C_5H_4)_2Fe_2(\mu\text{-}CO)_2(CO)P(OPh)_3]$ (**2**), in which even the migration of CO is blocked by $P(OPh)_3$.[7] This phenomenon has usually been attributed to PR_3 not being able to occupy the bridging positions between two metal centers and hence only being permanently bonded to one metal atom as a terminal ligand.



(R = OPh)

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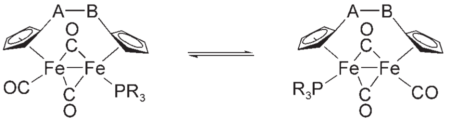
In the last few years however breakthroughs have been achieved in the isolation of stable complexes with bridging PR_3,[8,9] and more recently PR_3 migration between metal centers via bridging PR_3 intermediates or transition states has also been detected by dynamic NMR-spectroscopic studies of several systems, including a metal dimer $[(\eta^5\text{-}C_5Me_5)_2Ru_2(\mu\text{-}H)_2PR_3]$ (R = Me, Et, *i*Pr, Cy, Bz, OMe, OPh)[10] and metal clusters, such as $[PtRu_5(\mu_6\text{-}C)(CO)_{15}(PMe_2R)]$ (R = Ph and Me),[11a] and $[RuOs_3(\mu\text{-}H)_2(CO)_{12}(\mu_6\text{-}C)PPh_3]$.[11b] Even so, the inability of PR_3 to participate in the classical Adams–Cotton fluxional process is still generally accepted, and thus it has been difficult to classify PR_3 as a normal "fluxional ligand". Herein we report the first observation of PR_3 participation in the Adams–Cotton fluxional process, which occurs at such a slow rate that is not detectable by dynamic NMR spectroscopy.

We detected PR_3 migration by the simple strategy of using an asymmetric bridge connecting two cyclopentadienyl rings. This approach was found to be an ideal choice because other methods, such as introducing substituents onto the cyclopentadienyl rings of the symmetrically bridged derivatives such as **2**, could cause steric problems that hinder free migration of PR_3.[12] Although systems with symmetrical silicon or carbon bridges have been extensively studied in the past, complexes with asymmetric bridges have been seldom reported.[13,14] In the course of our studies into silicon–silicon bond activation by transition-metal complexes, $Me_2SiSiPh_2$ and CH_2SiMe_2 have been used as the bridging groups in the diiron complex, and the PR_3-substituted derivatives $[(\eta^5,\eta^5\text{-}C_5H_4Me_2SiSiPh_2C_5H_4)Fe_2(\mu\text{-}CO)_2(CO)PR_3]$ (R = OMe (**3a**), OEt (**3b**), Me (**3c**)) and $[(\eta^5,\eta^5\text{-}C_5H_4CH_2SiMe_2C_5H_4)Fe_2(\mu\text{-}CO)_2(CO)PR_3]$ (R = OMe (**4a**), OEt (**4b**), OPh (**4c**)) have been synthesized. These complexes are mixtures of *cis* (**3a′–c′** and **4a′–c′**) and *trans* (**3a″–c″** and **4a″–c″**) isomers (where *cis* and *trans* refer to the relationship between PR_3 and bridging group B, see Equation (1)). Fortunately, the pure *cis* or *trans* isomers could be successfully isolated by fractional crystallization of the mixtures at −30 °C, and their structures have been fully characterized by X-ray diffraction (see Supporting Information).

When the pure isomers were redissolved in solvent, it was surprising to find that they gradually transformed into the other isomer and ultimately resulted in an equilibrium mixture of the two isomers in a ratio of about 1:1 [Eq. (1)].



(1)

3a'	(A-B = $Me_2SiSiPh_2$, R = OMe)	**3a"**
3b'	(A-B = $Me_2SiSiPh_2$, R = OEt)	**3b"**
3c'	(A-B = $Me_2SiSiPh_2$, R = Me)	**3c"**
4a'	(A-B = CH_2SiMe_2, R = OMe)	**4a"**
4b'	(A-B = CH_2SiMe_2, R = OEt)	**4b"**
4c'	(A-B = CH_2SiMe_2, R = OPh)	**4c"**

Interestingly, this transformation is such a slow process that may be monitored by means of conventional ^1H NMR spectroscopy (Figure 1). This finding clearly demonstrates that PR_3 can freely migrate between two iron centers, and the previous inability to detect such PR_3 migration in the

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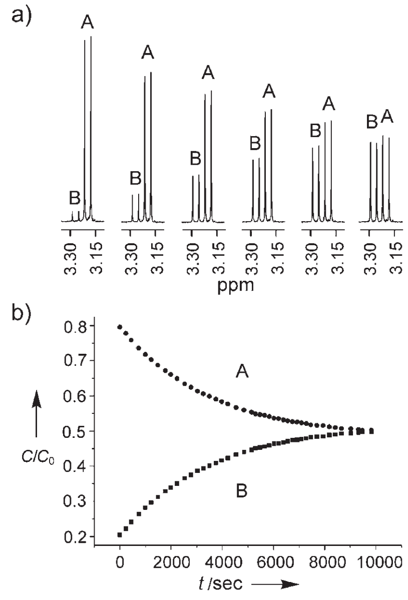
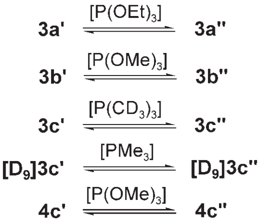


Figure 1. ^{1}H-NMR-spectroscopic monitoring of phosphorus-ligand migration. A **3a″**; B **3a′**. a) $P(OMe)_3$ signal change with time. From left: 7, 20, 40, 67, 105, and 201 min after re-dissolution of **3a″** in C_6D_6. b) Relative concentrations versus time for both isomers.

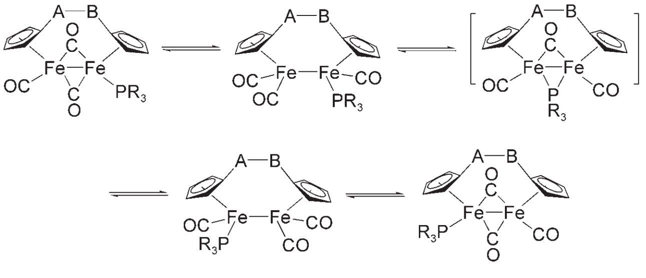
symmetrical systems such as **2** arises from the chemical equivalence of the two iron centers rather than the stability of the coordination bond of $P(OPh)_3$.

Running the migration in the presence of another free ligand, for example the reaction of **3a′** or **3b′**, that contain ligands $P(OMe)_3$ and $P(OEt)_3$, in the presence of the free ligands $P(OEt)_3$ and $P(OMe)_3$, respectively, gave no ligand-exchange products. The same result was observed for the complex **3c′** with ligand PMe_3 in the presence of the deuterated ligand $[D_9]PMe_3$, and vice versa. An experiment using complex **4c′** containing the ligand $P(OPh)_3$ in the presence of $P(OMe)_3$ also gave no exchange (Scheme 1). These results unambiguously rule out the possibility of ligand migration through dissociative release of PR_3 followed by its recoordination to the metal center.



$$\mathbf{3a'} \xrightleftharpoons{[P(OEt)_3]} \mathbf{3a''}$$
$$\mathbf{3b'} \xrightleftharpoons{[P(OMe)_3]} \mathbf{3b''}$$
$$\mathbf{3c'} \xrightleftharpoons{[P(CD_3)_3]} \mathbf{3c''}$$
$$\mathbf{[D_9]3c'} \xrightleftharpoons{[PMe_3]} \mathbf{[D_9]3c''}$$
$$\mathbf{4c'} \xrightleftharpoons{[P(OMe)_3]} \mathbf{4c''}$$

Scheme 1. PR_3 migration in the presence of another phosphorus ligand (shown in the square brackets), demonstrating that the latter did not exchange with the PR_3 ligand in the reaction substrates.



Scheme 2. Proposed mechanism for the migration of PR_3 between two metal centers via formation of a bridging PR_3 intermediate.

A nondissociative mechanism is therefore responsible for the migration of PR_3. Such a migration between two iron centers must pass through a bridging PR_3 intermediate or transition state, similar to the formation of bridging CO (Scheme 2). The existence of stable complexes and unstable intermediates or transition states having bridging PR_3 has already been established and theoretical calculations have also indicated that PR_3 should be able to form the bridging structures with pentacoordinate phosphorus.[8b,9,10] In fact, pentacoordination is not new in phosphorus chemistry.[15] Thus there should be little doubt about the formation of the bridging PR_3 during the PR_3 migration in the present systems, although it could not be detected by either IR or NMR spectroscopy.

To gain further insight into details of the migration process, the kinetics of the reaction were studied by ^{1}H NMR spectroscopy. The results showed standard first-order kinetics apply for both the forward and the reverse processes. The enthalpy of activation ($\Delta H^{\neq}$) for all the compounds studied were below 22.3 kcal mol^{-1} (Table 1), which is less than the energy needed for dissociation of CO[16] or PR_3,[17] and even for breaking the weakest Fe–Fe bond (ca. 27 kcal mol^{-1}).[18] This rules out the possibility of the involvement of such steps in the PR_3 migration process and therefore confirms the above mechanism that involves only concurrent migration of CO, which has a rather low energy barrier of approximately 11 kcal mol^{-1}; this is only half the height of the energy barrier for the present PR_3 migration.[6] Interestingly, the $\Delta H^{\neq}$ values are not very sensitive to the electronic effects of the alkyl and alkoxyl substituents of the small phosphorus ligands. This result is consistent with there being no obvious difference in related bond lengths and angles in the molecular structures of these complexes as determined by X-ray diffraction (Table 2). The only exception was that the larger ligand $P(OPh)_3$ in **4c**

Table 1: Activation parameters of phosphorus ligand migration determined by kinetic studies.

Entry	Reactions	Solvent	$\Delta H^{\neq}_1/\Delta H^{\neq}_{-1}$[a]	$\Delta S^{\neq}/\Delta S^{\neq}_{-1}$[b]	$\Delta G^{\neq}_1/\Delta G^{\neq}_{-1}$[c]
1	**3a′**⇄**3a″**	$[D_6]$benzene	21.0 ± 0.7/21.1 ± 0.6	−3.6 ± 2.2/−3.4 ± 2.0	22.0/22.1
2	**3a′**⇄**3a″**	[D]chloroform	20.1 ± 0.6/20.0 ± 0.6	−8.1 ± 2.1/−8.3 ± 2.1	22.5/22.5
3	**3b′**⇄**3b″**	$[D_6]$benzene	20.7 ± 0.6/20.6 ± 0.6	−5.6 ± 2.0/−6.2 ± 1.8	22.3/22.4
4	**3c′**⇄**3c″**	$[D_6]$benzene	18.4 ± 0.5/18.9 ± 0.5	−10.4 ± 1.7/−9.0 ± 1.7	21.5/21.6
5	**4a′**⇄**4a″**	$[D_6]$benzene	21.8 ± 0.3/21.8 ± 0.3	−2.8 ± 1.0/−2.8 ± 0.9	22.7/22.6
6	**4b′**⇄**4b″**	$[D_6]$benzene	22.2 ± 0.4/22.3 ± 0.4	−2.1 ± 1.3/−1.8 ± 1.2	22.8/22.8
7	**4c′**⇄**4c″**		[d]	[d]	[d]

[a] Units: kcal mol^{-1}. [b] Units: cal K^{-1} mol^{-1}. [c] at 298.2 K; units: kcal mol^{-1}. [d] Not determined as the reaction was too rapid to monitor by ^{1}H NMR spectroscopy.

could accelerate the rate of migration markedly, probably deriving from a steric effect, such that it could hardly be monitored by ^{1}H NMR spectroscopy.

Table 2: Selected bond lengths and angles as determined by X-ray diffraction[a]

Bond Lengths/ Angles[b]	**3a′**	**3b′**	**3c′**	**4a″**	**4b′**	**4c″**
Fe–Fe	2.5220(7)	2.5381(14)	2.5205(14)	2.5290(7)	2.5311(8)	2.516(2)
Fe–P	2.1287(10)	2.1409(18)	2.189(2)	2.1420(9)	2.1465(12)	2.113(3)
Si–Si	2.3969(12)	2.362(2)	2.460(3)			
C–Si[d]				1.870(3)	1.863(5)	–[c]
P–Fe–Fe	106.47(3)	103.85(5)	107.88(7)	105.76(3)	104.42(4)	104.50(8)

[a] For details of the X-ray diffraction studies, see Supporting Information. [b] Bond lengths [Å], angles [°]. [c] Not accurately determined owing to substantial thermal motion of the carbon atom. [d] on the bridge.

Use of a polar solvent did not significantly change the $\Delta H^{\ddagger}$ value (Table 1, entry 2), in agreement with formation of the nonpolar intermediates/transition states. Of particular note is the small negative entropies of activation ($\Delta S^{\ddagger}$) that have been observed, which is in accord with the nondissociative mechanism (in which the formation of bridging PR_3 restricts rotation of the M–P bonds, leading to an increase in order) rather than the dissociative one that would have large positive $\Delta S^{\ddagger}$ values.[10]

The results obtained show that PR_3 migration in the diiron complexes can in fact take place in a similar fashion to CO migration, except that a higher energy is required and as a result a slow migration rate is exhibited. This assertion is especially reasonable considering the relatively low—albeit well-established—ability of PR_3 to form bridging structures. The observation of slow migration of PR_3 indicates that such fluxional behavior in transition-metal complexes must occur much more extensively than has been detected using dynamic NMR-spectroscopic methods alone. The influence of this feature of PR_3 on the chemistry and properties of related systems, ranging from simple dimers through polynuclear clusters to nanocrystals of transition metals, will have to be considered in the future.[19] It must be noted that slow migration of chain-linked diphosphorus ligands, such as $Ph_2P(CH_2)_nPPh_2$, via bridging intermediates/transition states in metal clusters was reported very recently. Unfortunately, such migration only occurred for the chain length $n=2$ and not for $n=1$, 3, and 4. Such a strong dependence on the chain length indicates that the migration cannot be regarded as free migration of simple monophosphorus ligands PR_3.[20]

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