

enormous $P(C_6H_{11})_2$ groups in the equatorial positions.

Figure 4 shows the simulations of the variable-temperature spectra and yields a barrier of 10.8 ± 0.4 kcal mol⁻¹. One is tempted to propose that the rather similar values of ΔG^\ddagger for carbonyl migration and for phosphine rotation are not mere coincidence. Undoubtedly, the very large cone angle of tricyclohexylphosphine ($\approx 180 \pm 10^\circ$) causes steric problems and may severely restrict rotation not only of the phosphine but also of the cyclohexyl rings in the triply bridged isomer **3**. Molecular modeling studies on tricyclohexylphosphine itself suggest that rotation of a single ring is difficult and that correlated rotations of the rings are favored.¹² It is indeed possible that bridge opening to an isomer such as **5** provides release of steric strain and so facilitates phosphine rotation. Thus, the two fluxional processes, viz., carbonyl migration and phosphine rotation may be correlated but such a scenario is certainly not mandatory.

To conclude, we have shown that the exchange mechanism in **3** occurs via a completely bridge-opened structure in which local rotation of $Co(CO)_3$ vertices is rapid; thus these two carbonyl migration processes can be simulated by a single set of rate constants at a given temperature. To put these results in perspective, we note that in $Fe(CO)_3Co_2(CO)_6S$ the local rotation of the $Fe(CO)_3$ vertex can be slowed on the NMR time scale but rotation of the cobalt fragments cannot.¹³ This has been rationalized with the aid of molecular orbital calculations at the extended Hückel level.¹⁴ Interestingly, in $CpMo(CO)_2Co_2(CO)_6CR$ clusters (which have all-terminal ground-state structures) the rate of carbonyl migration between molybdenum and cobalt centers is controlled by the rate of $CpMo(CO)_2$ vertex rotation.¹⁵

(12) (a) Correlated rotation of the triphenylphosphine ligand in $[(C_6H_5)_3Fe(CO)(PPh_3)COCH_3]$ has recently been invoked; in this molecule, rotation about the Fe-P bond can also be slowed on the NMR time scale: Davies, S. G.; Derome, A. E.; McNally, J. P. *J. Am. Chem. Soc.* 1991, 113, 2854. (b) For a clear explication of dynamic gearing at the molecular level, see: Iwamura, H.; Mislou, K. *Acc. Chem. Res.* 1988, 21, 175.

(13) Aime, S.; Milone, L.; Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* 1977, 25, 103.

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Experimental Section

¹³C NMR spectra were recorded in CD_2Cl_2 at 125.7 MHz on a Bruker AM 500 spectrometer. Carbon-13 2D spectra were obtained at $-90^\circ C$ by using the standard NOESY pulse sequence, D1-90-D0-D9-90-FID. Spectra were acquired by using 16 scans for each of 256 FID's that contained 1024 points in the F2 dimension covering a spectral width of 6024 Hz. Delay D1 was 0.15 s, delay D0 was 3 μs , delay D9 was 10 ms, and the 90° pulse width was 5.7 μs . The F1 dimension was zero-filled to 512 points, and a Gaussian window function was applied in both dimensions during Fourier transformation using a line-broadening factor (LB) of 50 and a Gaussian broadening factor (GB) of zero.

NMR simulations were carried out by using the multisite EXCHANGE program generously provided by Professor R. E. D. McClung (University of Alberta at Edmonton). Molecular modeling studies were conducted by using the CHEMX modeling package.¹⁶

$CH_3CCO_3(CO)_6P(c-C_6H_{11})_3$ (**3**) was prepared following the method of Matheson et al.^{7b} and was enriched by stirring a methylene chloride solution of **3** under an atmosphere of ¹³CO for 1 week. ¹³C NMR spectrum of **3** ($-90^\circ C$): δ 233.24 [1], 230.95 [2], 204.68 [1], 200.44 [2], 198.76 [2] (Co carbonyls), 39.95 (CH₃), 33.82 [2], 29.41 [1] (C-1), 29.77 [2], 28.57 [2], 25.89 [2] (C-2), 27.73 [4], 25.29 [2] (C-3), 25.89 [2], 24.72 [1] (C-4). At $-10^\circ C$, δ 211.46 (Co-carbonyls), 40.95 (CH₃), 34.38 (d, C-1), 29.33 (C-2), 27.73 (d, C-3), 26.28 (C-4). The ¹³C assignments for the tricyclohexylphosphine ligand follow those given by Rügger for a series of platinum complexes for which ³¹P-coupled doublets are visible for C-1 and C-3.¹⁷

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Registry No. **3**, 22338-04-1.

(15) Sutin, K. A.; Li, L.; Frampton, C. S.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* 1991, 10, 2362.

(16) CHEMX, developed and distributed by Chemical Design Ltd., Oxford, U.K., 1986.

(17) Rügger, H. *Magn. Reson. Chem.* 1991, 29, 113.

Application of the Concerted Bridge Opening-Closing Mechanism to the Fluxionality of $[Fe_3(CO)_{10}(L)(CNCF_3)]$ ($L = CO, PMe_3, PET_3, P(OMe)_3, P(OEt)_3$)

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Summary: Recently, Lentz and Marschall have claimed to have discovered a new mechanism for the fluxionality of triiron carbonyl clusters. It is shown that a previously published mechanism involving concerted bridge opening and closing fits their data.

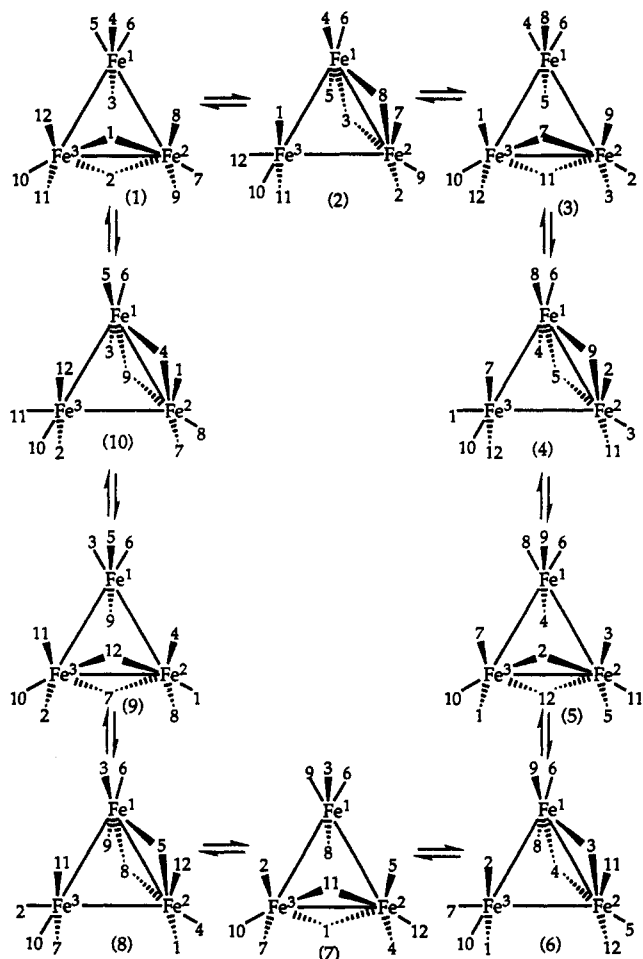
In a recent paper,¹ Lentz and Marschall claimed to have discovered a new mechanism for the fluxionality of triiron

carbonyl clusters and used the formalism of metal skeleton motion within the shell of ligands due to Johnson² to interpret their results. They claimed that "none of the mechanisms provided so far for the exchange process in $[Fe_3(CO)_{12}]$ fits the experimental spectra of $[Fe_3(CO)_{11}(CNCF_3)]$ and $[Fe_3(CO)_{10}(L)(CNCF_3)]$ ". This is incorrect. Their results can be fitted by a previously published mechanism³ which used the original formalism of carbonyl

(1) Lentz, D.; Marschall, R. *Organometallics* 1991, 10, 1487.

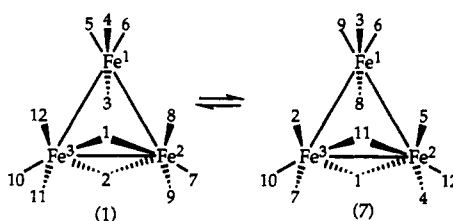
(2) See: Johnson, B. F. G.; Bott, A. *J. Chem. Soc., Dalton Trans* 1990, 2437 and papers referenced therein.

Scheme I. Low-Energy Concerted Bridge Opening-Closing Ligand Scrambling Mechanism for $[\text{Fe}_3(\text{CO})_{12}]$, Illustrated about One Pair of Fe-Fe Edges, Where the Numbers 1-12 Refer to the Ligands



migration over the metal skeleton due to Cotton.⁴ Lentz and Marschall referenced this paper³ in their paper but did not discuss it. The low-energy mechanism for carbonyl exchange in $[\text{Fe}_3(\text{CO})_{12}]$ and its derivatives has been shown to be a concerted bridge opening-closing mechanism.³ In $[\text{Fe}_3(\text{CO})_{12}]$, this mechanism can occur about any two pairs of Fe-Fe edges, resulting in complete carbonyl scrambling, but is illustrated for one pair of edges in Scheme I. In $[\text{Fe}_3(\text{CO})_{10}(\text{L})(\text{CNCF}_3)]$, $\text{L} = \text{PMe}_3$ or PET_3 , the structure observed in the X-ray structure and in the solution ¹³C NMR spectra is 1, with $\text{L}^1 = \text{CNCF}_3$ and $\text{L}^{10} = \text{L}$. Previous work has shown that for $[\text{Fe}_3(\text{CO})_{12-n}\text{L}_n]$, when $\text{L} = \text{a phosphorus ligand}$, the phosphorus ligand always remains equatorial.³ Thus, the presence of a phosphorus ligand at position L^{10} prevents ligand scrambling about the $\text{Fe}^1\text{-Fe}^3$ edge. Examination of the mechanism given in Scheme I shows that when the ligand scrambling occurs around the edges $\text{Fe}^1\text{-Fe}^2$ and $\text{Fe}^2\text{-Fe}^3$, then L^{10} (and L^6) remain equatorial. For the CNCF_3 ligand to return to the bridging position, the exchange has to progress as far as 7, giving the overall exchange shown in Scheme II.

Scheme II. Overall Low-Energy Concerted Bridge Opening-Closing Scrambling Mechanism for $[\text{Fe}_3(\text{CO})_{10}(\text{L})(\text{CNCF}_3)]$ ($\text{L}^1 = \text{CNCF}_3$, $\text{L}^{10} = \text{Phosphorus Ligand}$)



Although 7 is the mirror image of 1, when $\text{L}^1 = \text{CNCF}_3$ and $\text{L}^{10} = \text{phosphorus ligand}$, as far as carbonyl exchange in the NMR spectrum is concerned, this has no consequences, and the mechanism in Scheme II predicts the pairwise exchanges $\text{C}^2\text{O} \leftrightarrow \text{C}^{11}\text{O}$, $\text{C}^4\text{O} \leftrightarrow \text{C}^8\text{O}$, $\text{C}^5\text{O} \leftrightarrow \text{C}^9\text{O}$, and $\text{C}^7\text{O} \leftrightarrow \text{C}^{12}\text{O}$. Carbonyls C^3O and C^6O are unaffected. This is consistent with the ¹³C NMR spectra presented by Lentz and Marschall for 1, $\text{L}^1 = \text{CNCF}_3$ and $\text{L}^{10} = \text{PMe}_3$, PET_3 , $\text{P}(\text{OMe})_3$, and $\text{P}(\text{OEt})_3$. Scheme II produces the same ligand exchange as predicted by Lentz and Marschall using the Johnson formalism. It should be noted that the mechanism in Scheme I does not interconvert the two isomers observed for $\text{L} = \text{P}(\text{OMe})_3$ or $\text{P}(\text{OEt})_3$, but this interconversion can be achieved by the well-established merry-go-round mechanism.⁵

In the case of $[\text{Fe}_3(\text{CO})_{11}(\text{CNCF}_3)]$, there is higher symmetry, and the mechanism given in Scheme I can also be applied to the $\text{Fe}^1\text{-Fe}^3$ edge. Rather than enlarging Scheme I to accommodate the extra fluxional pathways, it can be noted that 1 now has a plane of symmetry through Fe^1 and ligands 1 and 2.⁶ Consequently, $\text{C}^5\text{O} \equiv \text{C}^6\text{O}$, $\text{C}^7\text{O} \equiv \text{C}^{10}\text{O}$, $\text{C}^8\text{O} \equiv \text{C}^{12}\text{O}$, and $\text{C}^9\text{O} \equiv \text{C}^{11}\text{O}$. When this condition is superimposed on the exchanges noted in Scheme II, there are two sets of exchanging carbonyls:

- i. C^2O , C^5O , C^6O , C^9O , and C^{11}O
- ii. C^4O , C^7O , C^8O , C^{10}O , and C^{12}O

C^3O does not exchange. This is consistent with the ¹³C NMR spectrum observed at 0 °C by Lentz and Marschall, which shows three carbonyl signals in the ratio 1:5:5. Above 0 °C, a second mechanism causes further exchange, presumably via the merry-go-round mechanism.⁵

The activation energy for the ligand scrambling in these CNCF_3 derivatives is higher than for the carbonyl analogues, where it is less than 6 kcal mol⁻¹. This is not surprising. It is possible that to open a CNCF_3 bridge could be energetically less favorable than opening a CO bridge, and the interconversion of 1 and 7 could involve some high-energy intermediates. None of the intermediates 2-6 or 8-10 are observed, and they therefore must be at least 1 kcal mol⁻¹ less stable than 1.

In conclusion, the variable-temperature ¹³C NMR spectra of $[\text{Fe}(\text{CO})_{10}(\text{L})(\text{CNCF}_3)]$, $\text{L} = \text{CO}$ or phosphorus ligand, are consistent with previously published mechanisms.

Registry No. $[\text{Fe}(\text{CO})_{11}(\text{CNCF}_3)]$, 92066-33-6; $[\text{Fe}(\text{CO})_{10}\text{PMe}_3(\text{CNCF}_3)]$, 130761-28-3; $[\text{Fe}(\text{CO})_{10}\text{PET}_3(\text{CNCF}_3)]$, 130761-29-4; $[\text{Fe}(\text{CO})_{10}\text{P}(\text{OMe})_3(\text{CNCF}_3)]$, 130797-36-3; $[\text{Fe}(\text{CO})_{10}\text{P}(\text{OEt})_3(\text{CNCF}_3)]$, 130761-27-2.

(3) Adams, H. A.; Bailey, N. A.; Bentley, G. W.; Mann, B. E. *J. Chem. Soc., Dalton Trans* 1989, 1831.

(4) Adams, R. D.; Cotton, F. A. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1975; p 489.

(5) Cotton, F. A.; Hunter, D. L. *Inorg. Chim. Acta* 1974, 11, L9.

(6) The consequences of the bent $\mu\text{-CNCF}_3$ ligand are ignored as they appear to have no effect on the exchange mechanism.