Organometallics **1992,** *11,* 477-481

E isomer 152 (33), 109 (30), 96 (20), 95 (100), 82 (30), 81 (63), 67 (44), exact mass 152.157; calcd for $C_{11}H_{20}$ 152.1566. Signals in the NMR spectra are assigned as follows. ^{1}H NMR: *Z* isomer δ 5.16 (m, 1), 2.65 (m, 1), 2.38–2.10 (m, 2), 2.06–1.93 (m, 2), 1.89–1.48 (m, 4), 1.33–1.28 (m, 2), 1.18–1.09 (m, 2), 0.93 (d, 3, J = 7 Hz), 0.88 (t, 3, J = 7 Hz); *E* isomer δ 5.10 (m, 1), 2.38–2.10 (m, 3), 2.06–1.93 (m, 2), 1.89–1.48 (m, 4), 1.33–1.28 (m, 4), 1.01 (d, 3, J = 7 Hz), 0.88 (t, 3, J = 7 Hz). ^{13}C NMR: *Z* isomer δ 147.9, 120.4, 35.1, 34.6, 33.3, 29.1, 28.8, 24.1, 22.5, 19.1, 14.1; *E* isomer δ 147.8, 119.4, 38.8, 35.6, 32.4, 32.0, 29.0, 24.0, 22.4, 20.7, 14.1.

Acknowledgment. This work was partially supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Departmental equipment grants aided in the purchase of the following: Varian XL-300 NMR (PHS-SID-RR-1882-01), Bruker AM-500 NMR (PHS-SID-RR-02858 and NSF-CHE-85-13707), and Kratos MS 80 mass spectrometers (NSF-CHE-81-11957).

Registry No. **1a**, 42049-41-2; **1b**, 136954-13-7; **1c**, 57718-12-4; **2a**, 94012-69-8; (*E*)-**2b**, 136954-14-8; (*Z*)-**2b**, 136954-15-9; **2c**, 57718-22-6; **3a**, 1942-46-7; **3b**, 2294-72-6; **3c**, 1129-65-3; **4a**, 53366-55-5; (*E*)-**4b**, 136954-16-0; (*Z*)-**4b**, 136954-17-1; **4c**, 4410-77-9; **7**, 136954-18-2; **8**, 34886-50-5; **10**, 136954-19-3; **11**, 4250-81-1; **13**, 5244-75-7.

Variable-Temperature One- and Two-Dimensional ^{13}C NMR Studies on $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$: Mechanism of Carbonyl Migration

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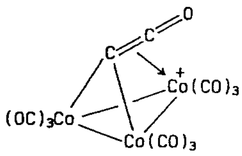
Summary: The 125.7-MHz ^{13}C NMR spectrum of $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ at −90 °C exhibits a 1:2:1:2:2 carbonyl pattern consistent with the triply bridged structure found in the solid state. The coalescence behavior of the ^{13}CO resonances can be simulated by invoking a mechanism in which a completely bridge-opened structure is required; local rotation of each $Co(CO)_3$ vertex is shown to be rapid. 2D-EXCHANGE spectroscopy is used as an independent probe for the fluxional processes and shows that, in accord with the bridge-opened model, all carbonyl sites do not exchange at the same rate. It is also demonstrated that rotation about the cobalt–phosphorus and P–C_{ipso} bonds is slowed on the NMR time scale.

The fluxional behavior of carbonyl ligands on metal cluster surfaces has attracted much attention for a considerable number of years. Some very fine experimental data have emerged; especially notable are the ingenious and elegant experiments carried out to elucidate the carbonyl scrambling mechanisms in heavy metal clusters.[1] Moreover, the thought-provoking ideas of Johnson and Benfield may give us cause to reevaluate our models of fluxionality in metal clusters.[2] Nevertheless, the situation is much less clear for carbonyl-capped tricobalt systems in which not only local rotation of $Co(CO)_3$ vertices but also intermetallic carbonyl migrations have such low barriers that the ^{13}CO NMR spectrum in solution is almost invariably a single line even at very low temperatures. Very recently, the 9-fold degeneracy of the carbonyl ligands in $[Co_3(CO)_9CC{=}O]^+$ (**1**) and in $Co_3(CO)_9CCH(C_6H_4Cl)_2$ (**2**) has been split to give in each case a 6:3 pattern at low temperature.[3,4] Although these results yield valuable structural information, they do not provide unequivocal answers to mechanistic questions.



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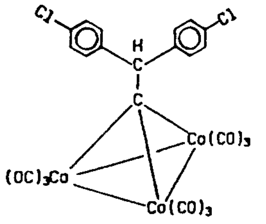
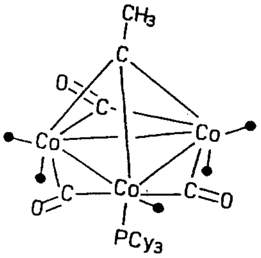


2

To our knowledge, the only other carbynyl–tricobalt cluster showing well-defined fluxional behavior is $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ which has the triple-bridged structure **3** in the solid state.[5] ^{13}C NMR measurements on **3** at 25 MHz suggested[6] that the low-temperature limiting spectrum would yield a 1:2:1:2:2 pattern for the carbonyl resonances, consistent with the solid-state structure. These data prompted us to initiate a study using high-field instrumentation which might allow a more complete analysis of the molecular dynamics of this system.



3

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(1) (a) Mann, B. E. *Adv. Organomet. Chem.* **1988**, *28*, 397 and references therein. (b) Strawczynski, A.; Ros, R.; Roulet, R. *Helv. Chim. Acta* **1988**, *71*, 867, 1885.

(2) (a) Benfield, R. E.; Johnson, B. F. G. *Transition Met. Chem. (London)* **1981**, *6*, 131. (b) Johnson, B. F. G.; Rodgers, A. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers Inc.: New York, 1990; pp 303-327 (see also references therein). (c) Hawkes, G.; Lian, L. Y.; Randall, E. W.; Sales, K. D. *J. Chem. Soc., Dalton Trans.* **1985**, 225.

(3) D'Agostino, M. F.; Mlekuz, M.; Kolis, J. W.; Sayer, B. G.; Rodger, C. A.; Halet, J.-F.; Saillard, J.-Y.; McGlinchey, M. J. *Organometallics* **1986**, *5*, 2345.

(4) Gates, R. A.; D'Agostino, M. F.; Sutin, K. A.; McGlinchey, M. J.; Janik, T. S.; Churchill, M. R. *Organometallics* **1990**, *9*, 20.

(5) Matheson, T. W.; Robinson, B. H. *Acta Crystallogr.* **1977**, *B33*, 1980.

(6) Matheson, T. W.; Robinson, B. H. *J. Organomet. Chem.* **1975**, *88*, 367.

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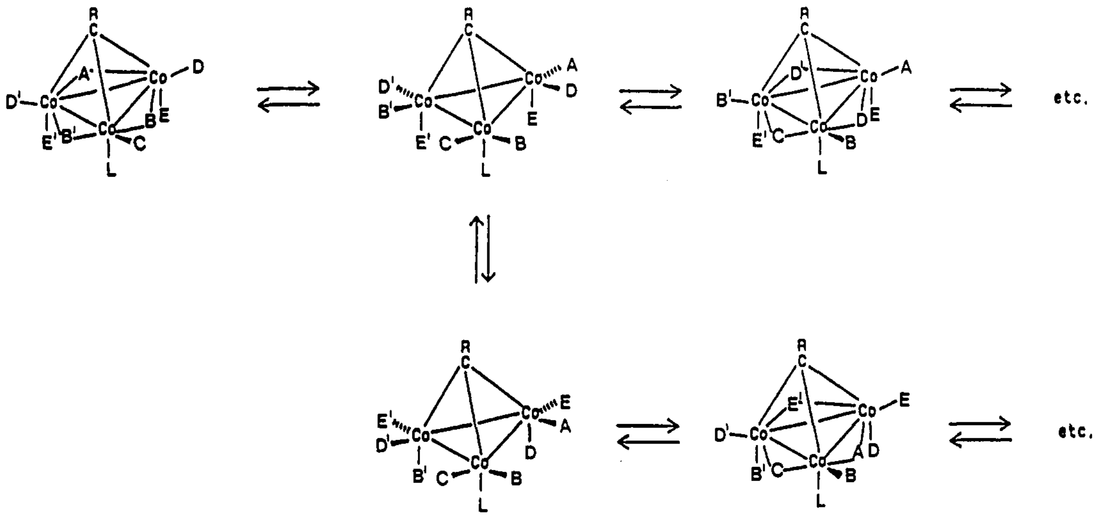
Scheme I. Proposed Scrambling Mechanism of the CO Ligands of 3[a]

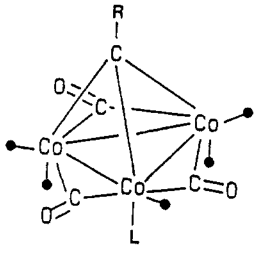


[a] Rapid local rotation can occur at the bridge–opened stage.

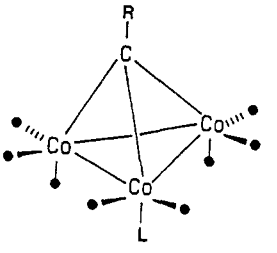
We now report the variable-temperature one- and two-dimensional ^{13}C NMR spectra of 3 obtained at 11.7 T (500 MHz for protons; 125.7 MHz for carbon-13 nuclei).

Results and Discussion

It has been established that the factors which affect the equilibrium between the bridged and nonbridged isomers 4 and 5 are rather subtle.[7] Nevertheless, it is generally true that bulky electron-donating phosphines favor the triple-bridged structure 4 which has been characterized crystallographically for the case where L = $P(c\text{-}C_6H_{11})_3$ (3).[5] Matheson and Robinson attempted to quantify the equilibrium ratios of 4:5 by using variable-temperature infrared spectroscopy and they concluded that for $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ (3) this ratio was 88:12 at 195 K.[6] We now report the variable-temperature ^{13}C NMR spectra of 3, as shown in Figure 1. These measurements confirm the preliminary report that the fluxionality of this complex can be slowed on the NMR time scale at low temperature. However, we found no NMR evidence which indicated the presence of any other isomer (such as 5). The relative intensities make assignment of the carbonyl peaks trivial except for the resonances at δ 200.4 and δ 198.8; these are clearly the terminal ligands (D and E) on the cobalts which do not bear the phosphine ligand. Although one cannot unequivocally assign a given resonance to the D site or the E environment, it turns out that this distinction is not crucial to the mechanistic argument.



4



5

Before attempting to simulate the set of experimental spectra shown in Figure 1, one must, of course, select a chemically reasonable scenario which ultimately equilibrates all the sites. The simple merry-go-round process,[8] shown in Scheme I, will eventually equilibrate the A, B, C, and D environments. Moreover, at the bridge-opened stage, rapid local rotation allows the axial ligands, viz. E and E′, to enter the sequence and so scramble all carbonyl sites.

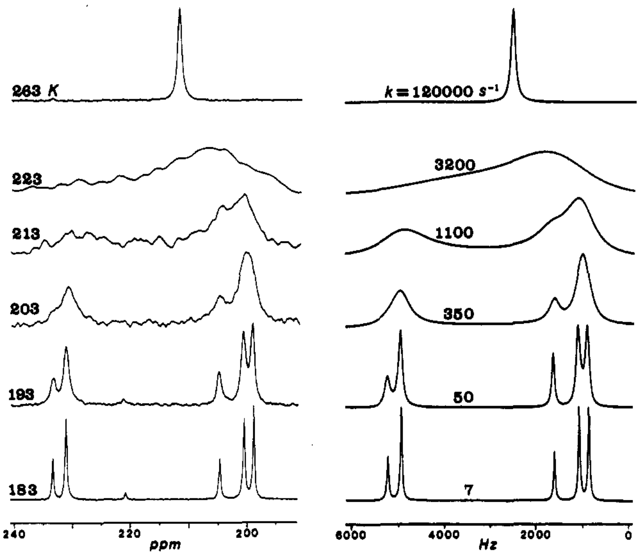


Figure 1. Experimental and simulated variable-temperature ^{13}C NMR spectra of $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ (3) in the metal carbonyl region.

In their early work, Matheson and Robinson proposed an alternative pathway which involved concerted conrotatory movement by ≈100° of each cobalt vertex so as to interconvert the bridged and nonbridged configurations.[6] This proposal would require the tricyclohexylphosphine ligand to oscillate between axial and equatorial positions. Such a process, in conjunction with local rotation of each cobalt vertex would allow each carbonyl access to all the other sites. However, we are less enthusiastic about moving the extremely bulky tricyclohexylphosphine ligand from its axial position and instead prefer the simple merry-go-round process.

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(7) (a) Brice, M. D.; Penfold, B. R.; Robinson, W. T.; Taylor, S. R. *Inorg. Chem.* **1970**, *9*, 362. (b) Matheson, T. W.; Robinson, B. H.; Tham, W. S. *J. Chem. Soc. A* **1971**, 1457.

(8) (a) Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1083. (b) Band, E.; Muetterties, E. L. *Chem. Rev.* **1978**, *78*, 639.

Table I. Exchange Matrix for Carbonyl Fluxionality in 3

	A	B	C	D	E
A	—	k	0	k	k
B	k	—	k	k	k
C	0	k	—	0	0
D	k	k	0	—	$2k$
E	k	k	0	$2k$	—

However, we wish to make the following points: (i) if the merry-go-round could operate rapidly *without the intermediacy of a completely nonbridged isomer* we should see rapid exchange among the A, B, C, and D environments and a subsequent slower collapse of peak E; (ii) in contrast, if the rate-determining step is the formation of the all-terminal isomer **5** (and local rotation of each $Co(CO)_3$ vertex has a very low barrier), then the rate for D ↔ E exchange will be *twice as fast* as the interconversions A ↔ D, A ↔ E, B ↔ D, B ↔ E, A ↔ B or B ↔ C. That is, each time the bridges open, half of the nuclei in the B environment exchange with C while the other 50% equilibrate with A, D, and E; concomitantly, the single A nucleus also scrambles with B, D, and E. But, and this is the crucial point, the entire populations of D and E are immediately rendered equivalent. Note that the C nucleus (which is attached to the same cobalt as the phosphine) cannot move directly onto the other cobalts without passing through one of the B sites. Hence, A ↔ C exchange must have the smallest rate constant. In light of these considerations, the experimental spectra in Figure 1 were simulated by using the exchange matrix shown in Table I for which the rate constant for D ↔ E interconversion was twice that for the others. Gratifyingly, there is an excellent correspondence between the experimental and calculated spectra and the resulting Arrhenius plot yields a value of 11.6 ± 0.3 kcal mol^{-1} for the activation energy. In the preliminary study[6] already referred to, the activation energy for carbonyl scrambling was estimated from a single coalescence temperature but such an approach is not valid for a multisite exchange process with unequal populations.

Although the line-shape simulations discussed above were in excellent agreement with the experimental spectra and any deviation from the exchange matrix in Table I (e.g., D ↔ E = $3k$) led to a significantly worse fit, we decided to seek independent evidence which might shed light on our mechanistic proposals. We therefore chose to look for direct evidence of the proposed mechanistic pathway and selected the 2D-EXCHANGE pulse sequence (NOESY)[9] for this purpose. The NOESY sequence, viz.

$$\pi/2\text{-}t_1\text{-}\pi/2\text{-}\tau_m\text{-}\pi/2\text{-}t_2$$

differs from the standard COSY experiment by the addition of a mixing time (τ_m) which provides an opportunity for a nucleus undergoing chemical exchange to migrate to another site. The experimental problem is to find an appropriate combination of mixing times and temperatures to detect different stages of the fluxional process. If the rate constant, k, is much less than $1/T_1$, then the frequency-labeled z magnetization will disappear before the nucleus has a chance to migrate;[10] in this particular instance, the presence of the quadrupolar cobalt nuclei reduces the carbonyl T_1's to less than 100 ms. On the other hand, we cannot raise the temperature to such a value that the rate constant causes us to lose the chemical shift difference between the exchanging sites. Figure 2a shows the result of an experiment carried out at 183 K but using a rather short mixing time of 7 ms. The only detectable process under these conditions is the D ↔ E exchange. Use of a slightly longer mixing time (τ_m = 10 ms) reveals a network of exchanging spins but not of A ↔ C, as shown by the cross-peaks indicated in Figure 2b. These experiments provide clear qualitative evidence that the exchange between the D and E sites is the fastest process while the

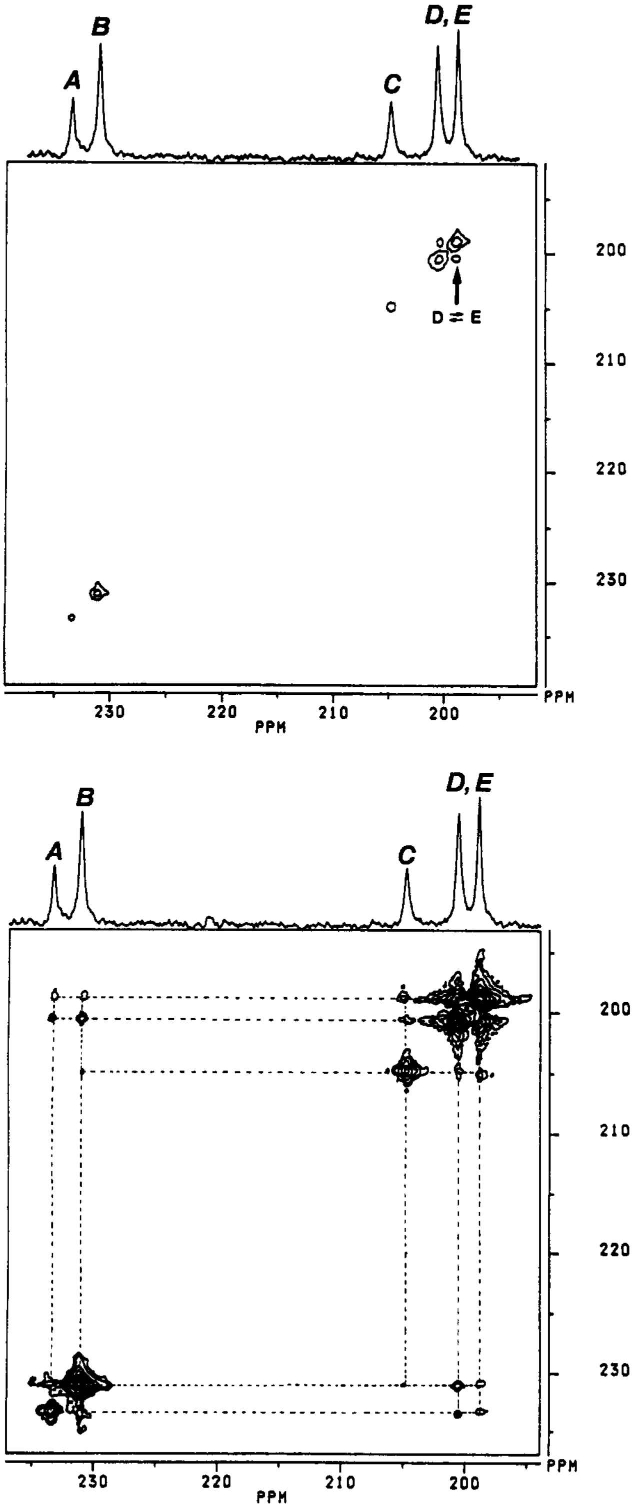

Figure 2. Contour plot representations of NOESY experiments at −90 °C; the mixing time (τ_m) is 7 ms in (a, top) and 10 ms in (b, bottom).

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[9] (a) Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 6441. (b) Huang, Y.; Macura, S.; Ernst, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5327.

[10] (a) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, U.K., 1987; pp 241. (b) For a superb example see: Ismail, A. A.; Sauriol, F.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1989**, *28*, 1007.

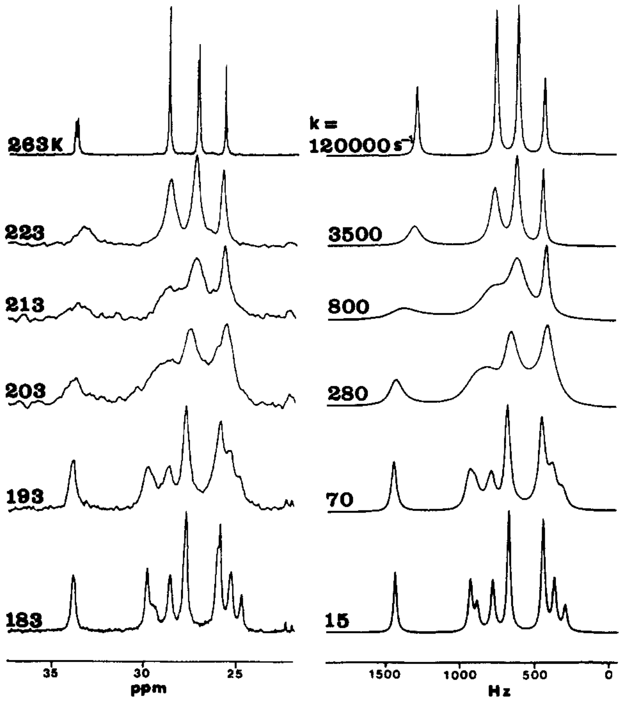

Figure 3. Experimental and simulated variable-temperature ^{13}C NMR spectra of $CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ (3) in the cyclohexyl ring region.

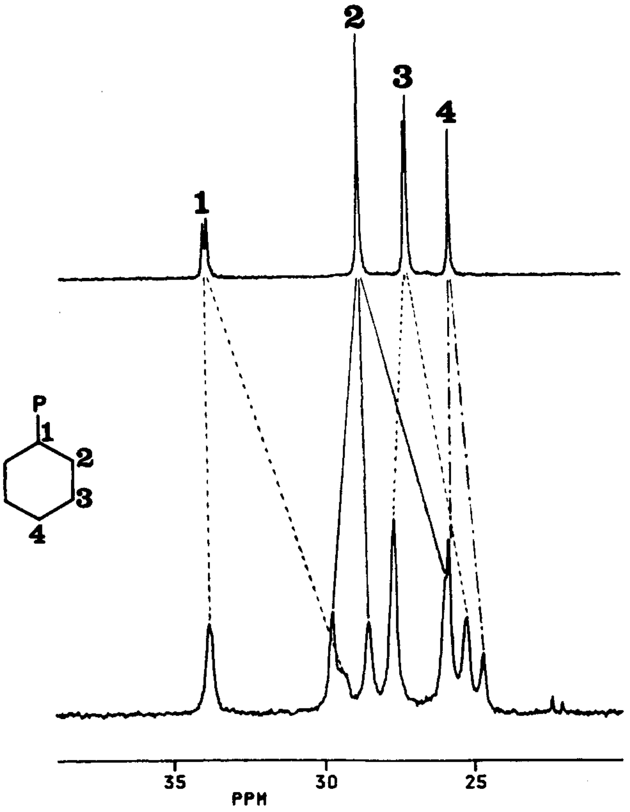

Figure 4. Peak coalescence pattern for the cyclohexyl carbons of 3.

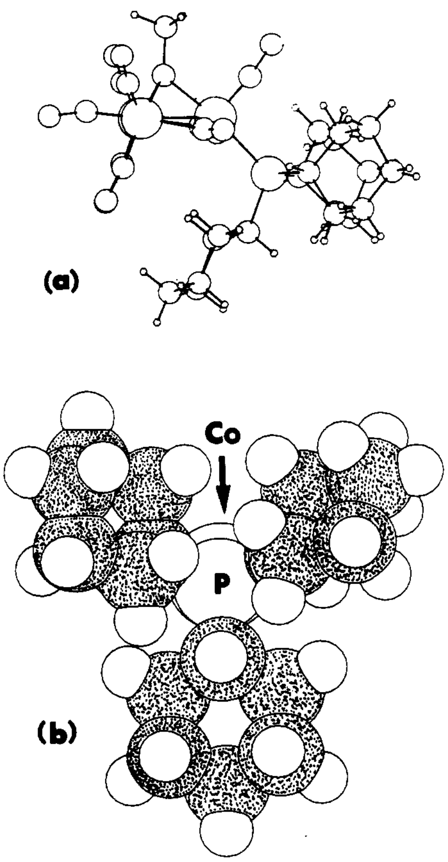

Figure 5. Views of the X-ray crystal structure of 3. (a) shows the chair conformations of the cyclohexyl rings while (b) is a view along the phosphorus–cobalt bond showing the relative orientations of the rings. (The atom coordinates are taken from ref 5.)

A ↔ C interchange is the slowest one. In principle, one could attempt to quantify the 2D-EXCHANGE data, as has been elegantly described by Orrell et al.[11] The experimental problem in this particular case is that, even at high field, the temperature range over which the chemical shifts remain distinct is only about 20 deg and so it is difficult to obtain good variable-temperature data.

It is also of interest to view the low-frequency (high-field) region of the ^{13}C spectra of 3 which depicts the resonances of the tricyclohexylphosphine ligand; as the temperature is lowered, these peaks exhibit clear decoalescence behavior. As shown in Figures 3 and 4, the C(1) and C(4) peaks are split 2:1, while the C(2) and C(3) resonances each yield 2:2:2 patterns. This is readily explicable in terms of the crystal structure of 3, which reveals effective C_s symmetry. At low temperature the local 3-fold symmetry of the phosphine ligand is broken, as rotation about the phosphorus–cobalt bond becomes slow on the NMR time scale. We see from Figure 5 (which depicts the conformation of 3 as established by X-ray crystallography[5]) that, as expected, the three cyclohexyl rings adopt chair conformations in which the phosphorus is positioned equatorially. Two of these cyclohexyl groups are related by the molecular mirror plane while the third ring straddles this plane. The former two rings are oriented such that half of each cyclohexyl fragment is *proximal* with respect to the tricobalt plane while the other edge of each ring is *distal*. Moreover, as shown in Figure 5, the axial proton at C(1) in the unique ring points inward toward the pseudo 3-fold Co–P axis while the corresponding axial H(1) atoms are directed outward in the other two cyclohexyl rings. Thus, simple rotation through 120° about the cobalt–phosphorus axis does not suffice to interconvert all the C(2) and C(3) sites; rotation about the C(1)–P bonds is also required. Of course, these rings cannot flip to the other chair since the conformations are locked in place by the

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[11] Abel, E. W.; Coston, T. P. J.; Orrell, K. G.; Sik, V.; Stephenson, D. *J. Magn. Reson.* **1986**, *70*, 34.

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 $\Delta G^{\ddagger}$ for carbonyl migration and for phosphine rotation are not mere coincidence. Undoubtedly, the very large cone angle of tricyclohexylphosphine (≈180 ± 10°) 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]

Experimental Section

^{13}C 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 °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]

$CH_3CCo_3(CO)_8P(c\text{-}C_6H_{11})_3$ (**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 ^{13}CO for 1 week. ^{13}C NMR spectrum of **3** (−90 °C): δ 233.24 [1], 230.95 [2], 204.68 [1], 200.44 [2], 198.76 [2] (Co carbonyls), 39.95 (CH_3), 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 °C, δ 211.46 (Co-carbonyls), 40.95 (CH_3), 34.38 (d, C-1), 29.33 (C-2), 27.73 (d, C-3), 26.28 (C-4). The ^{13}C assignments for the tricyclohexylphosphine ligand follow those given by Rüegger for a series of platinum complexes for which ^{31}P-coupled doublets are visible for C-1 and C-3.[17]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. L.L. is an Ontario Graduate Scholar and is also the recipient of a J. R. Longstaffe Scholarship; M.F.D. is an NSERC postgraduate scholarship holder. We also thank our colleague Professor D. R. Eaton for useful discussions and the referees for their helpful comments.

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

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(12) (a) Correlated rotation of the triphenylphosphine ligand in $[(C_5H_5)Fe(CO)(PPh_3)COCH_3]$ 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.; Mislow, K. *Acc. Chem. Res.* **1988**, *21*, 175.

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

(14) Malisza, K. L.; D'Agostino, M. F.; Sutin, K. A.; McGlinchey, M. J. Submitted for publication.

(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) Rüegger, 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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Received July 16, 1991

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 Johnson[2] 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 mechanism[3] which used the original formalism of carbonyl

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(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.

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