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An investigation of the barriers to trimethylenemethane (TMM) rotation in compounds of the type η^4-TMMFe(CO)$_2$L (L = ^{t}BuNC, AsPh$_3$, tertiary phosphines); examples of coordinated tertiary phosphine rotational isomerism

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Abstract

Variable temperature ^{1}H NMR studies of the compounds η^4-TMMFe(CO)$_2$L (L = PMe$_2$Ph, PMePh$_2$, PPh$_3$, PBz$_3$, ^{t}BuNC, AsPh$_3$, P(p-MeOC$_6$H$_4$)$_3$) have been carried out in order to determine the barriers to TMM rotation. It is found that the values of $\Delta G^\ddagger$ are lowered by good σ donor ligands L, the variation in $\Delta S^\ddagger$ being a more important factor than the variation in $\Delta H^\ddagger$. The compounds containing the ligands PMe$_2$Ph, PMePh$_2$, PCy$_2$Ph and PCyPh$_2$, with two different substituents, also exhibit conformational isomerism, as indicated by doubling of the carbonyl stretching bands in the IR spectra; MMX calculations confirm the identity of the conformations as the two possible staggered rotamers of C_1 and C_s symmetry.

We have recently reported the synthesis and characterization of a series of complexes of the type η^4-TMMFe(CO)$_2$L (η^4-TMM = {η^4-C(CH$_2$)$_3$}; L = ^{t}BuNC, tertiary phosphines) [1]. Of considerable interest in several cases were observations of temperature-dependent exchange broadening of the TMM resonances in the ^{1}H NMR spectra, attributed tentatively to restricted rotation of the TMM ligand. While fluxional processes involving TMM ligand rotation had been previously investigated for the TMM-substituted compounds, (RTMMFe(CO)$_3$ (R = COMe, CHOHHMe, CHMeOAc) [2], and TMMFe(CO)$_n$(PF$_3$)$_{3-n}$ [3], the rotational barriers found were considerably higher than those estimated by us on the basis of coalescence temperatures for the compounds η^4-TMMFe(CO)$_2$L [1]. Since theoretical considerations suggest that the phosphine-substituted compounds should exhibit higher barriers to TMM rotation [4], we have now carried out a much more detailed line-shape analysis of the temperature-dependent changes in the TMM resonances of the compounds η^4-TMMFe(CO)$_2$L (η^4-TMM = {η^4-C(CH$_2$)$_3$}; L = PMe$_2$Ph, PMePh$_2$, PCyPh$_2$, PCy$_2$Ph, PPh$_3$, PBz$_3$, ^{t}BuNC, AsPh$_3$, P(p-MeOC$_6$H$_4$)$_3$).

We also observed in several cases more than the anticipated pair of carbonyl stretching bands in the IR spectra, presumably attributable to rotational isomerism of the coordinated phosphines [1]. We now rationalize the effects of rotational isomerism of the ligands L on the IR spectra of the compounds η^4-TMMFe(CO)$_2$L (η^4-TMM = {η^4-C(CH$_2$)$_3$}; L = PMe$_2$Ph, PMePh$_2$, PCy$_2$Ph, PCyPh$_2$). Molecular mechanics calculations utilizing MMX, which has been shown to be particularly useful when applied to organometallic systems [5], provide relevant information concerning the relative energies of the various possible conformations.

1. Experimental details

The compounds η^4-TMMFe(CO)$_2$L (η^4-TMM = {η^4-C(CH$_2$)$_3$}; L = PMe$_2$Ph, PMePh$_2$, PCyPh$_2$, PCy$_2$Ph, PPh$_3$, PBz$_3$, ^{t}BuNC) were prepared as previously [1]. The new complexes η^4-TMMFe(CO)$_2$L (L = AsPh$_3$, P(p-MeOC$_6$H$_4$)$_3$) were prepared similarly as yellow, crystalline solids, and were characterized by IR (Table 1) and ^{1}H NMR spectroscopy (Table 2).

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TABLE 1. Carbonyl stretching frequencies of the compounds η^4-TMMFe(CO)$_2$L

L	ν(CO) (cm^{-1}) [a]
PCy_3	1986, 1928
PBz_3	1991, 1933
$PCyPh_2$	1991, 1987, 1934, 1931
PCy_2Ph	1992, 1988, 1933, 1930
P(p-MeOC$_6$H$_4$)$_3$	1994, 1938
PMe_2Ph	1996 (sh), 1992, 1939 (sh), 1935
PPh_3	1997, 1941
$AsPh_3$	1997, 1941
$PMePh_2$	1998 (sh), 1994, 1942 (sh), 1938
^{t}BuNC	2005, 1959

[a] In petroleum ether, b.p. 30–60°C.

IR spectra were run on a Bruker IFS-85 FTIR spectrometer at a resolution of 0.5 cm^{-1} utilizing, for variable temperature work, a Specac solution IR cell fitted with AgCl windows. The sample cell was placed within a Specac Variable Temperature Cell, the temperature being monitored to within ±1 K using a Specac Temperature Controller equipped with a copper–constantan thermocouple. The solution cell was fitted with a continuous flow-through unit which allowed it to be filled and flushed while in the VT cell. IR data from the carbonyl stretching region are presented in Table 1.

^{1}H NMR spectra were run on a Bruker AM-400 NMR spectrometer and, in one instance, on a Bruker HX-60 spectrometer. VT-NMR experiments were carried out on millimolar solutions of the compounds in toluene-d_8, the residual methyl protons in toluene-d_8 being used as a reference and assigned as δ 2.09 regardless of temperature. Total NMR line-shape analyses were carried out utilizing DNMR3 [6].

2. Results and discussion

2.1. Barriers to TMM rotation

Relevant ^{1}H NMR data are listed in Table 2, the TMM resonances being assigned as in the Newman diagram shown in Fig. 1. As mentioned previously [1], the TMM protons of most of the compounds appear as well-resolved resonances at room temperature, although the spectrum of η^4-TMMFe(CO)$_2$PBz$_3$ exhibits three broad TMM resonances of equal intensity. In the latter case, cooling of the NMR sample to 265 K resulted in well-resolved resonances from which the NMR parameters listed in Table 2 were extracted.

TABLE 2. ^{1}H NMR data for the compounds η^4-TMMFe(CO)$_2$L [a]

L	TMM resonances (δ)		
	$H_{a,a'}$	$H_{b,b'}$	$H_{c,c'}$
PBz_3	0.66 (dd)	1.32 (d)	1.12 (s)
PPh_3	1.05 (dd)	1.75 (d)	1.96 (s)
P(p-MeOC$_6$H$_4$)$_3$	1.19 (dd)	1.85 (d)	2.11 (s) [b]
$AsPh_3$	1.34 (d)	1.71 (d)	1.96 (s) [c]
^{t}BuNC	1.53 (d)	1.75 (d)	1.91 (s)
$PMePh_2$	1.07 (dd)	1.66 (d)	1.81 (s)
PMe_2Ph	1.03 (dd)	1.58 (d)	1.66 (s)

[a] In toluene-d_8. [b] $J(H_aH_b)$ 3.6 Hz; $J(PH_a)$ 9.5 Hz; δ (OMe) 2.99, J(PH) 8.6 Hz; δ (Ph) 6.39–7.36 (m). [c] $J(H_aH_b)$ 3.9 Hz; δ (Ph) 6.98–7.49.

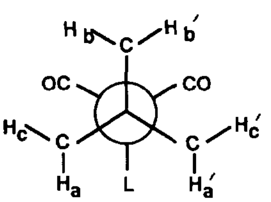

Fig. 1. Newman diagram for a compound η^4-TMMFe(CO)$_2$L viewed along the TMM–Fe axis.

In all cases, warming of a sample from a temperature at which the resonances were well resolved eventually led to coalescence of at least the relatively closely spaced doublet and singlet resonances of $H_{b,b'}$ and $H_{c,c'}$. In most cases, further warming also resulted in further coalescence with the higher field resonance of $H_{a,a'}$ to give a broadened resonance of line-width 10–15 Hz; in all cases, the temperature-dependent spectral changes were reversible. A typical example, involving the changes in the ^{1}H NMR spectrum of η^4-TMMFe(CO)$_2$PBz$_3$, is shown in Fig. 2. Although the rates of exchange were in all cases such that averaged, narrow resonances could not be achieved in toluene-d_8 at 400 MHz, a reasonably well resolved 60 MHz spectrum of η^4-TMMFe(CO)$_2$PBz$_3$ was obtained at 363 K. An averaged coupling J(HP) of 2.6 Hz was observed, confirming that the observed exchange process does not involve ligand dissociation.

Although the maximum number of spins which DNMR3 can accommodate is five, it was possible to take advantage of the high symmetry of the substituted TMM compounds (Fig. 1) to reduce the problem to 3- or 4-spin systems involving H_a, H_b, H_c and L. For purposes of the band shape simulations, exchange between the three proton sites was assumed to involve direct pair-wise 1,2-exchange between H_a and H_b, *etc.* Shown in Fig. 2 are the computer-generated spectra with "best-fit" values of k; the temperature dependencies of the latter were converted into activation parameters using the Eyring rate theory, and the results are shown in Table 3. In most cases, the values of $\Delta G^\ddagger$ obtained from the coalescence temperatures [1] are reasonably compatible with the results in Table 3. We also note that the generally negative values of $\Delta S^\ddagger$ argue strongly against the exchange processes involving ligand dissociation.

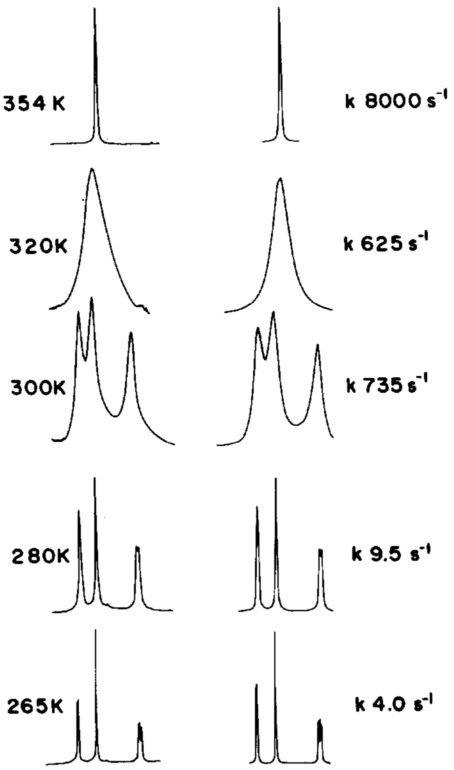

Fig. 2. ^{1}H NMR spectrum of η^4-TMMFe(CO)$_2$(PBz$_3$) in the temperature range 265–354 K; spectral simulations utilizing DNMR3.

The ligands are arranged in Table 3 in order of increasing $\Delta G^\ddagger$, although it is clear that the differences in $\Delta G^\ddagger$, except for the complex of ^{t}BuNC, are barely significant. There is also, for the Group 15 ligand donors, no clear correlation between ease of TMM rotation and any of $\Delta H^\ddagger$, $\Delta S^\ddagger$ or apparent steric requirements, as estimated on the basis of cone angles [7]. Indeed, the steric barrier to TMM rotation in a complex containing a relatively bulky phosphine, η^4-TMMFe(CO)$_2$PPh$_3$, was estimated utilizing MMX calculations [5] to be about 20 kJ mol^{-1}.

The much higher barrier found for η^4-TMMFe(CO)$_2$(^{t}BuNC), which seems to arise from both enthalpy and entropy factors, must therefore be a result of electronic factors arising from the relatively good π acceptor properties of the isonitrile ligand. Indeed, we note that the barrier calculated for η^4-TMMFe(CO)$_3$ utilizing extended Hückel calculations is about 90–100 kJ mol^{-1} [4], and that values of $\Delta G^\ddagger$, estimated on the basis of carbonyl ^{13}C resonances of the TMM-substituted compounds (RTMMFe(CO)$_3$ (R = COMe, CHOHHMe, CHMeOAc), are about 75 kJ mol^{-1} [2], significantly higher than the barriers found here for all but the isonitrile complex.

TABLE 3. Activation parameters for TMM rotation in the compounds η^4-TMMFe(CO)$_2$L

L	$\Delta G^{\ddagger\ a,b}$	$\Delta H^{\ddagger\ b}$	$\Delta S^{\ddagger\ c}$
PBz$_3$	62±4	63±3	2±3
PPh$_3$	65±4	59±2	−31±4
P(p-MeOC$_6$H$_4$)$_3$	68±4	63±3	−17±3
PMePh$_2$	69±1	65±1	−14±1
PMe$_2$Ph	70±3	64±2	−21±2
AsPh$_3$	72±6	62±5	−33±5
^{t}BuNC	91±6	67±4	−80±8

[a] At 298 K. [b] In kJ mol^{-1}. [c] In J mol^{-1} K^{-1}.

Following this line of thinking, we find that while the barriers to TMM rotation appear to correlate approximately inversely with σ donor ability, as shown by comparison of values of $\Delta G^\ddagger$ (Table 3) with the carbonyl stretching frequencies (Table 1), the differences are not, in fact, significant. However, it is reasonable that better σ donors would weaken the TMM–iron bond, thus facilitating TMM ligand rotation, and we note that the compound (η^4-TMM)Fe(PMe$_3$)$_3$ readily ejects the TMM diradical in solution to form the product of dimerization, 1,4-dimethylenecyclohexane [1]. It seems likely that the PMe$_3$ ligands behave as excellent σ donors, and thus that the barrier to rotation of TMM in this particular compound would be exceptionally low. Indeed, we have synthesized the relatively unstable (η^4-TMM)Fe(CO)$_2$(PMe$_3$) (ν(CO) = 1994, 1937 cm^{-1}), and find that coalescences of the TMM ^{1}H resonances occur at temperatures comparable to those of (η^4-TMM)Fe(CO)$_2$(PBz$_3$). On the other hand, spin-magnetization transfer experiments have established a lower limit of 95 kJ mol^{-1} for the barrier to TMM rotation in (η^4-TMM)Os(CO)$_2$(PPh$_3$), consistent with the expected relatively strong TMM–Os linkage [8].

Our findings that the barriers decrease as the σ bonding ability of L increases is in apparent conflict with the results of extended Hückel calculations, which predict the reverse trend [4]. A similar discrepancy between experimental findings and calculated barrier has been noted for the electronically very similar series of complexes (η^4-diene)Fe(CO)$_2$L (L = CO, tertiary phosphines) [9], but satisfactory rationalizations of the correlations do not yet appear to be available.

2.2. Conformational isomerism

Relevant IR data are presented in Table 1, where it is seen that the IR spectra of complexes in which the ligand L exhibits at least three-fold symmetry exhibit only two well-resolved carbonyl stretching bands, while the spectra of complexes of tertiary phosphines containing two different substituents exhibit two pairs of carbonyl stretching bands of roughly comparable intensities (see Fig. 3 for an example). A variable temperature IR experiment on a solution of η^4-TMMFe-

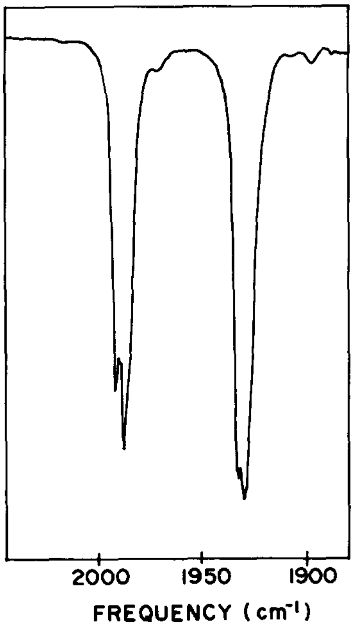

Fig. 3. Carbonyl stretching bands of η^4-TMMFe(CO)$_2$PCy$_2$Ph.

(CO)$_2$PCy$_2$Ph in 2-methylpentane showed that the relative intensities of the two pairs of carbonyl stretching frequencies varied little in the temperature range 200–298 K.

The doubling of absorption bands observed here is commonly associated with conformational (rotational) isomerism [5a,b], and the Newman diagrams of Fig. 4 illustrate the two most likely rotamers for the compounds under consideration here although we cannot assign either pair of absorptions to a particular rotamer. It is clear, however, that the compounds (η^4-TMM)Fe(CO)$_2$L (L = ^{t}BuNC, PPh$_3$, P(o-MeOC$_6$H$_4$)$_3$, PBz$_3$, AsPh$_3$) would exist in only one such staggered rotamer, in which case only a single pair of carbonyl stretching bands would be observed, as is the case. MMX calculations [5] were carried out for the compound (η^4-TMM)Fe(CO)$_2$(PMe$_2$Ph) using essentially the bond lengths and angles reported previously for the compound (η^4-TMM)Fe(CO)$_2$(PCy$_2$Ph) [1]. As anticipated, the two staggered structures of Fig. 4 were found to represent local minima, the difference in energy being about 1 kJ mol^{-1}, consonant with the experimental results although the calculated difference is not significant.

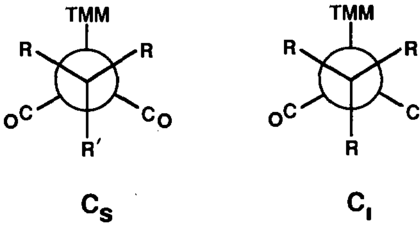

Fig. 4. Newman diagram for a compound η^4-TMMFe(CO)$_2$PR$_2$R′ viewed along the Fe–P axis.

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