Organonitrogen Groups in Metal Carbonyl Complexes. Part V.[1] ‡ Fluxional Behaviour of Aza-allyl/allene † Complexes

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Variable-temperature ^1H n.m.r. studies of the complexes $[(\pi\text{-}C_5H_5)M(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}]$ (M = Mo or W), showed the molecules to be fluxional, the observed temperature dependance being consistent with the occurrence of two distinct averaging processes within the aza-allyl/allene ligand. Further structural information was obtained from the ^1H n.m.r. spectra of the compounds $[(\pi\text{-}C_5H_5)Mo(CO)_2\{(R'C_6H_4)(R''C_6H_4)CNC(R'C_6H_4)(R''C_6H_4)\}]$ (R′ = p-Me, R″ = p-OMe or H) which showed that at low temperatures, certain orientations of the CR_2 groups with respect to the rest of the ligand are preferred. Kinetic measurements made from the ^{19}F n.m.r. spectra of the compounds $[(\pi\text{-}C_5H_5)M(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}]$ (M = Mo or W) gave values for E_a of 11·6 and 6·8 kcal/mol respectively.

MANY π-allyl complexes exhibit fluxional behaviour in solution as shown by their temperature-dependent ^1H n.m.r. spectra, although there appears to be much controversy in the literature as to the mechanisms by which the observed exchange processes occur and the intermediates involved.[2] Similar behaviour has been observed for the aza-allyl/allene complexes described below, and it is relevant to mention here the various bonding types and the proposed mechanisms for the fluxional changes of the related π-allyl groups.

π-Allyl complexes may be classified into two categories —the symmetric type characterised by an AM_2X_2 spectrum at low temperature, and the asymmetric type which has an AGMPX type spectrum at low temperature indicating that the terminal carbon atoms differ in their bonding to the metal. An AX_4 type spectrum is often observed for both types at elevated temperatures due to exchange of *syn-* and *anti*-protons, *i.e.* exchange of protons (1) and (2), and (3) and (4) in Figure 1.

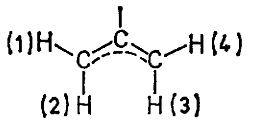
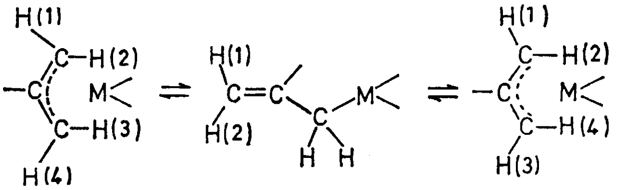


FIGURE 1

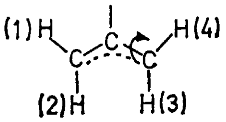
Three mechanisms have been proposed. The first and most popular is of the ' π–σ ' type, involving reversible interconversion between the two π-allyl forms *via* a σ-bonded intermediate [Figure 2(a)].[3]

syn-anti-Exchange may occur also *via* rotation about the C–C bonds of the skeleton while the allyl group remains π-bonded to the metal[4] [Figure 2(b)], although it would seem that this type of rotation is only really plausible for the specific examples quoted,[5] *e.g.* $Zr(allyl)_4$ and $Hf(allyl)_4$, and has no general applicability.

A third mechanism has been postulated[6] to account for the observations in compounds of the type [(allyl)Pd(amine)Cl] in which a broadening of the *anti*-proton



(a) Interconversion of protons (3) and (4) *via* a σ-intermediate



(b) *syn-anti*-Exchange *via* C┈┈C bond rotation

FIGURE 2

signals is observed while the *syn*-proton signals remain sharp, *i.e.* a process not involving *syn–anti*-exchange. It is thought that a ' flip ' movement (Figure 3) may be

FIGURE 3

involved [analogous to the equilibria found in cyclohexanes] about the C_1–C_3 axis, going through a transition state in which C_1, C_2, C_3, and Pd are co-planar, *i.e.* a σ–σ-bonded transition state.

In the case of asymmetric π-allyl compounds, *e.g.*

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† Throughout this paper the nomenclature of the organonitrogen group $[R_2CNCR_2]$ has been based on structurally related carbo-groups. The term aza-allyl refers to the group when the R_2C planes are planar [*cf.* the isoelectronic allyl group, $R_2CC(H)CR_2$], and the term aza-allene to the group when the R_2C planes are perpendicular. The latter group is formally derived from $[R_2C{=}\overset{+}{N}{=}CR_2]$, the dialkylideneammonium ion, which is isoelectronic and isostructural with allenes, $R_2C{=}C{=}CR_2$.

‡ Part IV, ref. 9.

[1] H. R. Keable and M. Kilner, *Chem. Comm.*, 1971, 349.

[2] K. Vrieze, H. C. Volger, and P. W. N. M. van Leeuwen, *Inorg. Chim. Acta Rev.*, 1969, **3**, 109, and references therein.

[3] (*a*) K. Vrieze and H. C. Volger, *J. Organometallic Chem.*, 1967, **9**, 537; (*b*) J. Powell and B. L. Shaw, *J. Chem. Soc.* (*A*), 1967, 1839; (*c*) G. L. Statton and K. C. Ramey, *J. Amer. Chem. Soc.*, 1966, **88**, 1327, 4387; (*d*) P. Corradini, G. Maglio, A. Musco, and G. Paiaro, *Chem. Comm.*, 1966, 618.

[4] J. K. Beconsall, B. E. Job, and S. O'Brien, *J. Chem. Soc.* (*A*), 1967, 423.

[5] F. A. Cotton, J. W. Faller, and A. Musco, *Inorg. Chem.*, 1967, **6**, 179.

[6] P. Ganis, G. Maglio, A. Musco, and A. L. Segre, *Inorg. Chim. Acta*, 1969, **3**, 266.

$(\pi\text{-}C_4H_7)PdCl(Ph_3P)$[7] and $(\pi\text{-}C_4H_7)Pd(OAc)(Ph_3P)$,[8] a coalescence of H(3) and H(4) only is observed while H(1) and H(2) remain sharp [Figure 2(a)]. In this case the 'π–σ' reaction is really the only possibility, the σ-bonded intermediate being formed preferentially by one end of the allyl group.

Our n.m.r. studies of a series of aza-allyl/allene complexes $[(\pi\text{-}C_5H_5)M(CO)_2\{R_2CNCR_2\}]$ (M = Mo or W) (R = aryl groups) show that at low temperatures, an asymmetric π, or σ–π, aza-allyl structure is adopted and that the averaging processes observed occur *via* the 'π–σ' mechanism.

RESULTS AND DISCUSSION

The complexes studied in this work, their carbonyl stretching frequencies and mass spectroscopic data are recorded in Table 1, and limited ^1H n.m.r. data are given in Table 2. Aza-allyl/allene complexes are the products of an unusual reaction between $[(\pi\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo or W) and a lithioketimine $[LiN{:}CR_2]$ (1 : 2 molar ratio), one nitrogen being lost along with a carbonyl group as a cyanate ion. A possible mechanism for the reaction has been discussed in an earlier paper.[9] The first complex of this type, $[(\pi\text{-}C_5H_5)Mo(CO)_2(Ph_2CNCPh_2)]$, was a derivative of diphenylketimine, but since the most useful technique to investigate the precise nature of the bonding is undoubtedly n.m.r. spectroscopy, the phenyl substituents were not amenable, unfortunately, to this type of study. Use of $Bu^t{}_2C{:}NLi$ in the preparative reaction resulted only in the formation of $[(\pi\text{-}C_5H_5)M(CO)_2N{:}CBu^t{}_2]$,[10] and indeed only aza-allyl/allene complexes with aryl substituents have been so far prepared.

TABLE 1

I.r. and mass spectroscopic data for aza-allyl/allene complexes

Complex	ν_{CO} (cm^{-1})(KBr disc)		m/e P^+ [a]	m/e $(P\text{-}CO)^+$ [a]	m/e $(P\text{-}2CO)^+$ [a]
$(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}$	1936s	1836s	621	593	565
$(\pi\text{-}C_5H_5)W(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}$	1934s 1931s	1815s [9,b] 1830s	707	679	651
$(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})(p\text{-}MeOC_6H_4)CNC(p\text{-tolyl})\text{-}(p\text{-}MeOC_6H_4)\}$	1930s	1831s	653	625	597
$(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})(Ph)CNC(Ph)(p\text{-tolyl})\}$	1924s	1841s	593	565	537
$(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}$	1962s 1954s	1883s [b] 1857s	837	809	781
$(\pi\text{-}C_5H_5)W(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}$	1963s 1954s	1880s [b] 1866s	923	895	867

[a] Refers to ^{98}Mo or ^{184}W. [b] Two isomers exist in the solid state—see ref. 9.

TABLE 2

^1H [a] and ^{19}F [b] N.m.r. data for aza-allyl/allene complexes

Complex	Temp.	τ(Ph) [c]	$\tau(C_6H_5)$	τ(MeO)	τ(Me)	p.p.m. (CF_3)
$(\pi\text{-}C_5H_5)Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$	−20°	2·92(16)	5·54(5)		7·49(3), 7·73(3), 7·82(3), 7·86(3)	
	10	2·92(16)	5·40(5)		7·49(3), 7·80(9)	
	70	2·92(16)	5·32(5)		7·72(12)	
$(\pi\text{-}C_5H_5)W(CO)_2[p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$	−20	2·92(16)	5·45(5)		7·48(3), 7·71(3), 7·81(3), 7·85(3)	
	10	2·92(16)	5·40(5)		7·49(3), 7·80(9)	
	70	2·92(16)	5·32(5)		7·71(12)	
$(\pi\text{-}C_5H_5)Mo(CO)_2[(p\text{-}MeOC_6H_4)(p\text{-tolyl})CNC\text{-}(p\text{-}MeOC_6H_4)(p\text{-tolyl})]$	−40	2·90	5·39, 5·48, 5·51	6·11, 6·27, 6·40, 6·45	7·46, 7·70, 7·79, 7·86	
	10	2·90	5·36, 5·47	6·12, 6·37	7·47, 7·78	
	70	2·90	5·42	6·33	7·71	
$(\pi\text{-}C_5H_5)Mo(CO)_2[(p\text{-tolyl})(C_6H_5)CNC\text{-}(p\text{-tolyl})(C_6H_5)]$	−40	2·85	5·46, 5·49, 5·55, 5·58		7·52, 7·75, 7·84, 7·88	
	10	2·85	5·43, 5·54		7·53, 7·82	
	70	2·85	5·43		7·74	
$(\pi\text{-}C_5H_5)Mo(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$	−20					62·23(3), 62·79(3), 62·90(3), 63·44(3)
	20		5·32(5)			62·67(6), 63·01(3) 63·56(3)
	60					62·95(12)
$(\pi\text{-}C_5H_5)W(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$	−35					62·58(3), 63·06(3), 63·21(3), 63·76(3)
	−5		5·40(5)			62·86(6), 63·20(3) 63·76(3)
	60					63·10(12)

[a] CS_2 Solution. [b] Toluene solution, p.p.m. values rel. to $CFCl_3$. [c] Centre of multiplet.

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[7] K. Vrieze, A. P. Praat, and P. Cossee, *J. Organometallic Chem.*, 1968, **12**, 533.

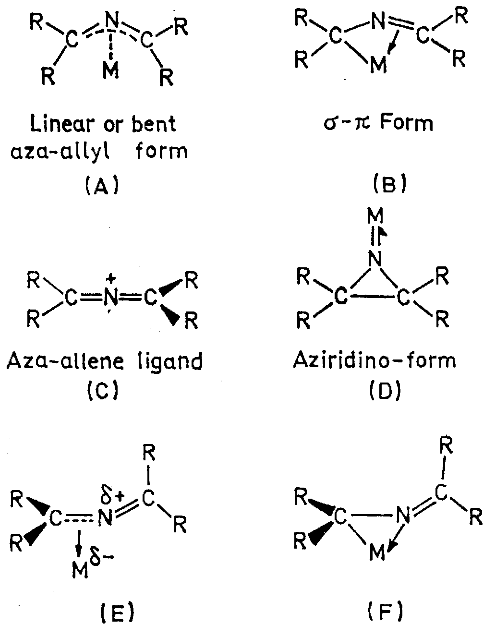
[8] P. W. N. M. van Leeuwen and A. P. Praat, *J. Organometallic Chem.*, 1970, **21**, 501.

[9] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153.

[10] M. Kilner and C. Midcalf, *J. Chem. Soc.* (*A*), 1971, 292.

We chose therefore to study complexes in which the aryl groups have suitable n.m.r. probes as *para*-substituents.

Several bonding modes of the ligand may be envisaged as shown in Figure 4. The symmetric π-aza-allyl group (Figure 4A) may be linear or bent depending on the extent to which the nitrogen lone pair is utilised in the bonding. All R groups would be in the same plane. The asymmetric π-aza-allyl group (Figure 4B) would have one end of the ligand co-ordinated more strongly to the metal than the other end, the structure shown representing an extreme. Again all four R groups lie in the same plane. Bonding of the π-aza-allene ligand (Figure 4C) would be expected to be of the mono-olefin type through one of the double bonds (as is found in many of the known π-allene complexes), with the unco-ordinated CR_2 group bent away from the metal.[11] Here the R groups would be in perpendicular planes. *X*-Ray crystallographic data show the complex $[(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}]$ to have an organo-nitrogen group with the *p*-tolyl substituents in perpendicular planes and a CNC angle of 128°.[12] Although the ligand in this complex may be considered as a π-aza-allene group (Figure 4E), alternatively the bonding may be represented as in Figure 4F involving σ-bonding of the carbon atom to the metal and bonding to nitrogen through the lone pair of electrons. This represents the extreme situation in which carbon–nitrogen bonding is reduced to a bond order of 1. The aziridine structure (Figure 4D) may be ruled out for all the complexes due to the lack of a diagnostic i.r. absorption in the 850—900 cm^{-1} region [13] and on the basis of the n.m.r. data.



Linear or bent aza-allyl form (A)

σ-π Form (B)

Aza-allene ligand (C)

Aziridino-form (D)

(E)

(F)

FIGURE 4
Possible structures for $(\pi\text{-}C_5H_5)M(CO)_2(R_2CNCR_2)$

Our n.m.r. results suggest that all the complexes have a significantly different structure in solution from that of $[(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}]$ in the solid state.

Variable-temperature studies between −20 and +70° showed the molecules to be fluxional. Relevant data are shown in Figure 5 for $[(\pi\text{-}C_5H_5)W(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}]$. At low temperature there are four signals of equal intensity due to the CH_3 protons, indicating that all four methyl groups are non-equivalent and that the terminal skeletal carbon atoms are unequally bound to the metal. Warming to 10° caused two signals (τ 7·71 and 7·85) to broaden, whilst the other two remained fairly sharp, before coalescing to a signal which is superimposed on the signal originally at τ 7·80. Thus two signals of intensity ratio 1 : 3 result. At 70° these signals coalesce to a broader time averaged signal at the mean (τ 7·71) of the four original signals, indicating that all four methyl groups are equivalent on the n.m.r. time scale. All these changes are completely reversible. This type of temperature dependence is very similar to that found for the asymmetric π-allyl compounds described above [7,8] and we conclude therefore that our low-temperature results are consistent only with an aza-allyl group with non-equivalent skeletal carbon atoms (Figure 6A and B). Coalescing of signals at +10° is interpreted as detachment of the C=N π-system from the metal and rotation of the –N=C(tolyl)$_2$ moiety about the C–N single bond (Figure 6C), thus causing R^3 and R^4 to

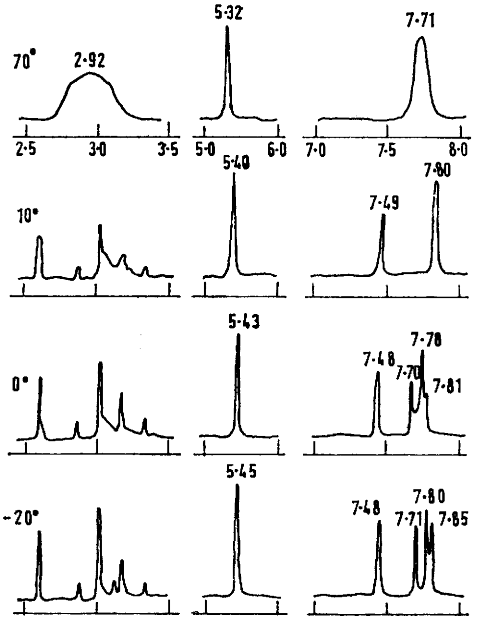


FIGURE 5 ^{1}H n.m.r. spectra for $(\pi\text{-}C_5H_5)W(CO)_2[(p\text{-}MeC_6H_4)_2CNC(p\text{-}MeC_6H_4)_2]$ in CS_2

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[11] T. G. Hewitt and J. J. De Boer, *J. Chem. Soc.* (*A*), 1971, 817; J. A. Osborne, *Chem. Comm.*, 1968, 1231.

[12] H. M. M. Shearer and J. D. Sowerby, personal communication.

[13] T. B. Jackson and J. O. Edwards, *Inorg. Chem.*, 1962, **1**, 398.

be equivalent. Construction of reasonable models based upon the available crystallographic data for the molybdenum complex indicates that such a rotation is sterically possible as the planes containing the phenyl rings can be twisted to any suitable angle, allowing free rotation to occur.

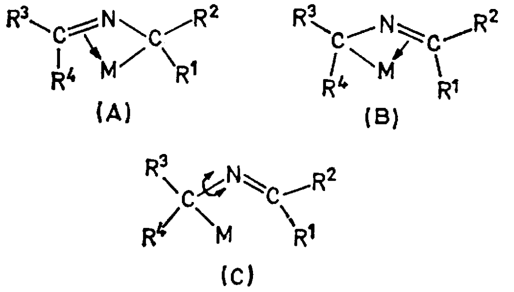


FIGURE 6

On warming to 70° interchange of σ–π bonding is thought to occur (Figure 6A and B) together with the rotation process, producing four equivalent groups. Confirmation of this latter mechanism has been obtained by studying the variable temperature n.m.r. spectrum of $[(\pi\text{-}C_5H_5)Mo(CO)_2\{(p\text{-}MeOC_6H_4)(p\text{-}MeC_6H_4)CNC(p\text{-}MeC_6H_4)(p\text{-}MeOC_6H_4)\}]$ for which the n.m.r. probes are a methoxy and a methyl group at each end of the ligand. At higher temperatures two broad time averaged signals are observed, one arising from the methoxy- and one from the methyl groups. The low-temperature spectrum is shown in Figure 7, the methoxy-resonances being to lower field. Four distinct signals are observed for both the methyl and methoxy-groups, the integration indicating six protons of each type. At low temperatures all four possible orientations of the aza-allyl ligand are therefore frozen out. Thus, each end of the ligand must become free from the metal at some stage to allow the rotational process to occur at each end, *i.e.* we have interchange of σ–π bonding as postulated.

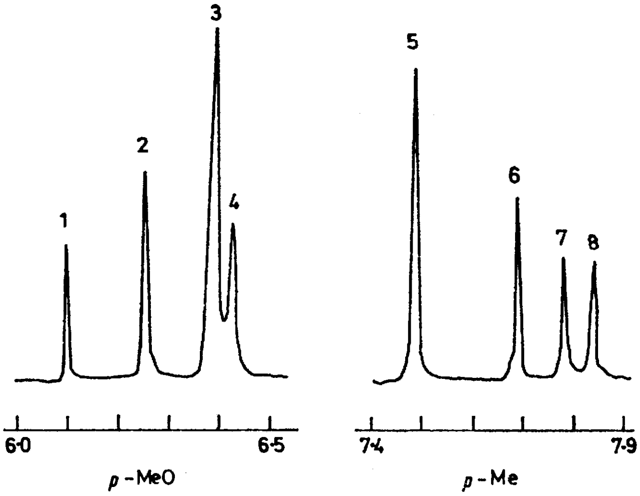
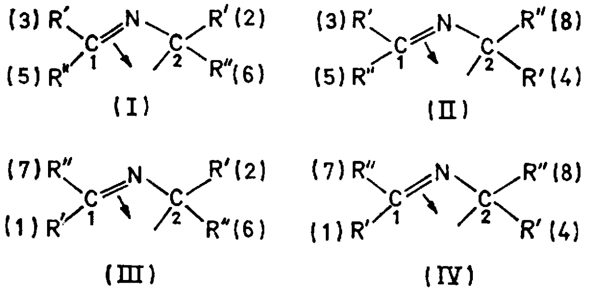


FIGURE 7 ^{1}H N.m.r. spectrum for $(\pi\text{-}C_5H_5)Mo(CO)_2[R'R''CNCR'R'']$ in CS_2 at −40° ($R' = p\text{-}MeOC_6H_4$, $R'' = p\text{-}MeC_6H_4$)

An additional point of interest to note from Figure 7 is that the signals within each group are not all of equal intensity. This implies that at low temperatures certain orientations of the CR_2 groups with respect to the rest of the molecule are preferred, and allows assignment of each of the four signals to a particular R group on the ligand to be made. The four possible orientations of the ligand are shown in Figure 8.

Construction of suitable models, based on the crystal structure described earlier shows that the *para*-substituents do not interact sterically with the $(\pi\text{-}C_5H_5)\text{-}M(CO)_2$ part of the molecule during the rotational process. Any possible steric interaction between the ligand and the $(\pi\text{-}C_5H_5)M(CO)_2$ moiety would involve the phenyl rings.



$R' = p\text{-}MeOC_6H_4$, $R'' = p\text{-}MeC_6H_4$
FIGURE 8

The models also show that during the rotational process significant interaction is possible between the *p*-MeO groups at each end of the ligand. Thus, the structure most likely to be adopted in the absence of rotation is the one in which *p*-MeO groups are furthest away, both from each other and the *p*-Me groups (Figure 8I). The ^{1}H n.m.r. results indicate that rotation of the $-N{=}CR_2$ unit causes signals due to R groups on C(2) (Figure 8) to coalesce, and these are peaks 2 and 4, 6 and 8 in Figure 7. On the basis of these data and the relative intensities of the signals, assignment of each signal to a substituent at a particular position on the ligand can be made. We therefore assign peaks 3 and 5 (Figure 7) to R′ and R″ respectively on C(1) (Figure 8I) peaks 2 and 6 (Figure 7) to R′ and R″ respectively on C(2) (Figure 8I). Hence peaks 1 and 4 (Figure 7) refer to R′ on C(1) and C(2) respectively (Figure 8IV) and peaks 7 and 8 (Figure 7) to R″ on C(1) and C(2) respectively (Figure 8IV). The signals arising from the substituents in the various positions in the structures of Figure 8 are indicated by numbers in parentheses referring to signals in Figure 7.

If these assignments, based upon steric arguments, are correct, then by putting $R' = C_6H_5$ in Figure 8, *i.e.* replacing the *p*-MeO substituents by H, the most favourable structure at low temperature would be Figure 8IV, with *p*-Me groups furthest away from each other, reducing any steric interactions between them. Thus we would expect the new intensity pattern of the methyl resonances at low temperature to be qualitatively very similar to the pattern observed for the *p*-MeO resonances in Figure 7. If there is no steric interaction between the *p*-Me groups, then four peaks of equal intensity should result. The spectrum obtained at −40° for $R' = C_6H_5$ and $R'' = p\text{-}MeC_6H_4$ is shown in Figure 9, and indeed the intensity pattern of the methyl resonances is in excellent agreement with the predictions.

The ^1H n.m.r. results have been interpreted on the basis of a σ–π type of bonding mode (Figure 4B) for the aza-allyl ligand, and the first coalescence of signals arising from detachment of the C=N π-system from the metal and rotation of the $-N{=}CR_2$ unit about the C–N single bond. The strength of the interaction between the metal and what would effectively be a lateral C=N-system will be reflected in the activation energy for the rotational process, and consequently attempts have been made to determine the kinetics of the process.

Inspection of the spectra of all the complexes described showed that (*a*) the separation between the coalescing peaks was too small (*ca.* 8 Hz) to allow accurate measurements to be made, and (*b*) the presence of a third methyl signal between the two, made measurements impossible. Introduction of CF_3 groups into the *para*-positions of all four R groups however solved both problems. The separation at low temperature between the coalescing signals increased, as expected, to *ca.* 30 Hz and fortuitously neither of the remaining CF_3 signals interfered.

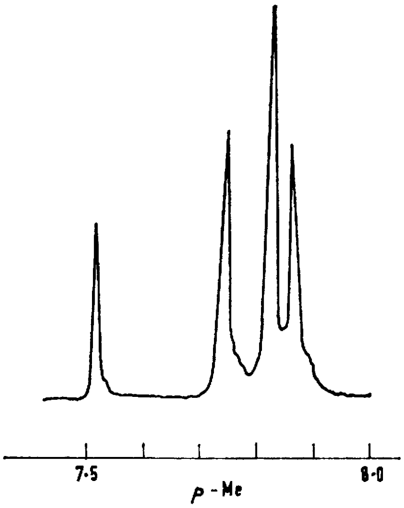


FIGURE 9 ^1H n.m.r. spectrum for $(\pi\text{-}C_5H_5)Mo(CO)_2[R'R''\text{-}CNCR'R'']$ in CS_2 at −40° ($R' = C_6H_5$, $R'' = p\text{-}MeC_6H_4$)

Relevant spectral details are shown in Figure 10. A similar temperature dependence to that already described for the *p*-tolyl derivative is observed, indicating that we are considering similar rotational processes. Activation energies were calculated by two independent methods, the peak separation method of Gutowsky[14] and the intensity ratio method described by Rogers and Woodbrey[15] (see Experimental section). Good agreement between the methods was obtained and the results are summarised in Table 3.

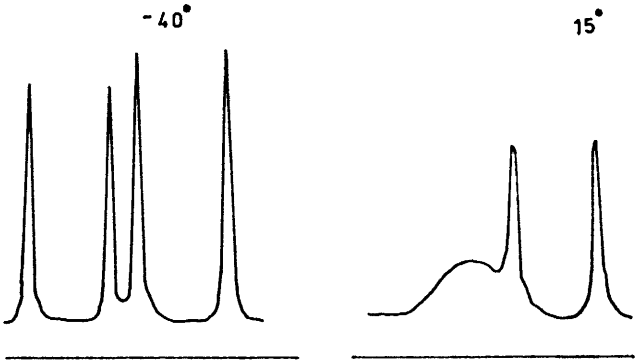


FIGURE 10 ^{19}F n.m.r. spectra for $(\pi\text{-}C_5H_5)Mo(CO)_2[(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2]$ in toluene

TABLE 3

Activation parameters for $(\pi\text{-}C_5H_5)M(CO)_2[(p\text{-}CF_3C_6H_4)_2\text{-}CNC(p\text{-}CF_3C_6H_4)_2]$ (M = Mo, W)

M = Mo: $E_a = 11{\cdot}6 \pm 1{\cdot}2$ kcal/mol
$\log_{10}A = 10{\cdot}8 \pm 1{\cdot}0$
M = W: $E_a = 6{\cdot}8 \pm 0{\cdot}5$ kcal/mol
$\log_{10}A = 7{\cdot}2 \pm 0{\cdot}4$

Comparable activation energy values for similar processes in related π-allyl systems are in the range 7—20 kcal/mol.[3a]

The values for the aza-derivatives are consistent with the contention that the activation energy results predominantly from metal–ligand interaction, rather than steric inhibition of rotation. If the latter were operative, then similar activation energies would be expected for the molybdenum and tungsten compounds, owing to the similarity in size of the two central atoms—covalent radii have been estimated as 1·61 Å for molybdenum[16] and 1·58 Å for tunsten[17]—resulting in similar molecular dimensions. It would appear therefore that the interaction between the metal and the C=N π-system is considerably stronger for molybdenum. Unfortunately no appropriate bond-energy data are available for molybdenum- or tungsten–nitrogen bonds, but the order observed is in notable contrast to the observed trend for metal-carbonyl bond energies, *i.e.* W–CO > Mo–CO.[18]

EXPERIMENTAL

π-Cyclopentadienyltricarbonyl-molybdenum and -tungsten halides were prepared by standard methods.[19] Hydrocarbon solvents and diethyl ether were dried over extruded

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sodium and monoglyme freshly distilled from lithium aluminium hydride. Carbon disulphide for n.m.r. measurements was distilled on to P_2O_5 and freshly distilled when required. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with rigorous exclusion of oxygen.

Spectra.—I.r. spectra in the range 4000—250 cm^{-1} were recorded with a Perkin-Elmer 457 spectrophotometer and mass spectra obtained with an A.E.I. MS9 instrument at 70 eV and an accelerating potential of 8 kV. Samples were inserted directly into the ion source at temperatures between 80 and 220°. ^1H and ^{19}F N.m.r. spectra were recorded at 60 or 56·4 MHz respectively with a Varian A56/60D spectrometer equipped with the Varian variable-temperature controller. Temperature calibration was by means of the standard Varian methanol sample. Spectra were obtained in CS_2 solution except for the fluorine-containing complexes which were obtained in toluene.

Analyses.—Carbon, hydrogen, and nitrogen were determined with a Perkin-Elmer 240 Elemental Analyser.

The preparation and characterisation of $(\pi\text{-}C_5H_5)M(CO)_2$-$[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$ (M = Mo, W) have been described in an earlier paper.[9] For the other complexes a similar method was employed, differing only in the preparation of the lithio-ketimine solutions which previously had been prepared from the ketimine and n-butyl lithium. The following method was devised for the preparation of lithio-ketimine solutions from readily available starting materials, utilising the method of metal–halogen exchange. Typically, an aryl bromide (R′Br) (4 mmol) was dissolved in diethyl ether (50 ml) and cooled in liquid nitrogen. A solution of Bu^nLi (4 mmol) in hexane (1·25 ml) was added by syringe and the solution was warmed to room temperature with stirring. Change of colour indicated reaction to be occurring, and the solution was stirred for 30 min to ensure complete equilibration (for aryl bromides and n-butyl-lithium the equilibrium position favours almost complete formation of the aryl-lithium compound). The solution was cooled again in liquid nitrogen and a solution of an aryl nitrile (R″CN) (4 mmol) in diethyl ether (5—10 ml) was added by syringe. An orange or red colour developed rapidly indicating formation of the lithio-ketimine; the solution was warmed to room temperature and stirred for *ca.* 20 min. Reaction with $[(\pi\text{-}C_5H_5)M(CO)_3Cl]$ at room temperature, and the initial work-up procedure are as described in ref. 9. Crystallisation at 0° from hexane or ether–hexane mixtures gave the following products of the type $(\pi\text{-}C_5H_5)M(CO)_2[R'R''CNCR'R'']$: (i) R′ = p-$MeOC_6H_4$, R″ = p-MeC_6H_4, M = Mo: m.p. 86—88° (Found: C, 68·35; H, 4·9; N, 2·2%. $C_{37}H_{33}MoNO_4$ requires C, 68·1; H, 5·1; N, 2·15%); (ii) R′ = C_6H_5, *R″* = p-MeC_6H_4, M = Mo: m.p. 183—184° (Found: C, 71·4; H, 4·95; N, 2·25%. $C_{35}H_{29}MoNO_2$ requires C, 71·0; H, 4·9; N, 2·35%); (iii) R′ = R″ = p-$CF_3C_6H_4$, M = Mo, m.p. 163—164° (Found: C, 52·9; H, 2·5; N, 1·7; F, 26·8%. $C_{37}H_{21}F_{12}MoNO_2$ requires C, 53·2; H, 2·5; N, 1·7; F, 27·3%); (iv) R′ = R″ = p-$CF_3C_6H_4$, M = W: m.p. 153—154° (Found: C, 48·0; H, 2·5; N, 1·52%. $C_{37}H_{21}F_{12}NO_2W$ requires C, 48·1; H, 2·3; N, 1·52%).

Activation energies, E_a, were obtained from measurements of the rate of internal rotation ($\frac{1}{2}\tau$) at a series of temperatures by fitting the data to the Arrhenius equation: $\log_{10}(\frac{1}{2}\tau) = \log_{10}A - E_a/2{\cdot}303\,RT$.

Values of E_a and the frequency factor, $\log_{10} A$, were derived from linear plots of $\log_{10}(\frac{1}{2}\tau)$ *vs.* $10^3/2{\cdot}303RT$ by the method of least squares. Values of τ at individual temperatures were obtained by two independent methods. That described by Rogers and Woodbrey [15] relates τ to the ratio (r) of maximum to central minimum v-mode intensities of the coalescing doublet by the equation

$$\tau \mathrm{d}v = \pm \frac{1}{\pi\sqrt{2}} \cdot [r \pm (r^2 - r)^{\frac{1}{2}}]^{\frac{1}{2}} \text{ for } \pi\sqrt{2}\,\tau \mathrm{d}v > 1$$

where dv is the chemical shift difference (Hz) between the two signals, and the effect of overlap of the components of the doublet is negligible, in the absence of rotational averaging. The method developed by Gutowsky and Holm [14] relates τ to the separation (Hz) between the components of the coalescing doublet at various temperatures, by the equation:

$$\mathrm{d}v_e = \left(1 - \frac{2}{\tau^2 \mathrm{d}v^2}\right)^{\frac{1}{2}} . \mathrm{d}v \text{ for } \tau\,\mathrm{d}v > \sqrt{2}$$

where dv is as above and the same conditions as to overlap apply. dv_e Is the experimentally observed separation.

A major drawback of this latter method becomes apparent when the value of dv is not constant with respect to temperature, *i.e.* the separation in the absence of rotation increases with decreasing temperature with no further decrease in linewidth.[20] This has the effect of increasing the range in which the rate appears to be changing and results in correspondingly smaller values of the activation energy. Such a problem was encountered in our measurements and the initial calculations showed large discrepancies between the two methods, owing to the value of dv being taken at too low a temperature. However, use of the value of dv obtained from the temperature at which no further line narrowing was apparent, gave results from the two methods which agreed within experimental error. The limits of E_a and $\log_{10} A$ were calculated for 90% confidence using conventional statistical methods.[21]

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