E.S.C.A. Studies of Some Transition-metal Carbonyl Complexes containing Organonitrogen Ligands

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E.s.c.a. spectra have been obtained for complexes of the type π-$C_5H_5M(CO)_2N{:}CR_2$ (I) and π-$C_5H_5M(CO)_2R_2$-$CNCR_2$ (II) (M = Mo or W; R = *p*-tolyl or *p*-$CF_3{\cdot}C_6H_4$). The observed binding energies have been used, in conjunction with other spectroscopic data, to discuss structure and bonding in these complexes and the isomeric forms of (II). A correlation between metal binding energies and the stretching frequencies of attached carbonyl groups has been found.

THE advantage of e.s.c.a.[1,2] over other spectroscopic techniques is that in principle it can provide data on the electronic environment of each constituent atom of a molecule and this makes it particularly attractive for studying structure and bonding. Such an application, relating to the nature of attachment of some organonitrogen groups to transition metals in some organometallic complexes, is now reported.

E.s.c.a. studies of some transition-metal carbonyls and π-cyclopentadienyls [3,4] have already gone some way to resolving problems relating to the electronic structure of the latter complexes, whilst a study of 8-hydroxyquinoline complexes of uranium(IV) demonstrated [5] the relative ease with which information on ligand bonding modes could be obtained.

The range of binding energies for N1*s* core levels in commonly encountered situations is fairly large (*ca.* 10 eV),[6,7] hence significant shifts can be expected upon co-ordination of ligands through nitrogen. Two ligand systems, the methyleneamino- ($R_2C{:}N$–) [8] and the aza-allyl/allene (R_2CNCR_2) [9] groups, have been investigated and each has the possibility of bonding in various ways. Two forms of the complex [π-$C_5H_5W(CO)_2$(*p*-tolyl)$_2$CNC-(*p*-tolyl)$_2$] have been isolated, which are thought to

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[8] M. Kilner and J. N. Pinkney, *J. Chem. Soc.* (*A*), 1971, 2887.

[9] K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc.* (*A*), 1970, 2279.

differ only in the nature of attachment of the organonitrogen group to the metal. The *para*-substituents of the aryl groups have a profound effect on the course of the reactions involving methyleneamino-derivatives and these electronic effects together with structural forms adopted by the ligands have been investigated by e.s.c.a.

EXPERIMENTAL

Spectra were recorded on an A.E.I. ES100 electron spectrometer with Mg-$K_{\alpha 1,2}$ radiation. Samples were studied as powders pressed on double sided scotch tape. Even though the percentage of nitrogen in some compounds is very low satisfactory spectra were always obtained.

Corrections for charging effects, typically <1 eV, were made as follows. All compounds contained *p*-tolyl or *p*-$CF_3{\cdot}C_6H_4$ groups which dominate their C1*s* spectra. $PhCH_3$ and $PhCF_3$, studied as thin condensed films on gold, under which conditions charging effects are minimised (<0·3 eV), gave the binding energies:[10] $PhCH_3$: C1*s* (centroid) = 285·0 eV and $PhCF_3$: C1*s* (centroid) = 286·3 eV (Ph), 293·8 eV ($-CF_3$), F1*s* = 690·8 eV. Under these conditions and those used for this investigation the Au$4f_{7/2}$ core level at 84·0 eV binding energy, used as reference, had a half-width of 1·15 eV. The C1*s* centroid for compounds with *p*-tolyl groups was, therefore, referenced to 285·0 eV and the F1*s* peak for the compounds with *p*-$CF_3{\cdot}C_6H_4$ groups referenced to 690·8 eV. For the latter compounds the C1*s* peaks arising from $-C_6H_4-$ and $-CF_3$ groups then occurred at 286·1 eV and 293·8 eV (binding energies) respectively in satisfactory agreement with the values from $PhCF_3$. The time-independent nature of the spectra and visual examination of the samples after removal from the spectrometer indicated that radiation damage was insignificant.

TABLE 1

Molecular core binding energies/eV

	C1*s*	F1*s*	N1*s*	Mo3$d_{5/2}$	W4$f_{7/2}$
π-$C_5H_5Mo(CO)_2$[NC(*p*-tolyl)$_2$]	_285·0_	—	398·4	229·0	—
π-$C_5H_5W(CO)_2$[NC(*p*-tolyl)$_2$]	_285·0_	—	398·8	—	31·6
π-$C_5H_5W(CO)_2$[NC(*p*-$CF_3{\cdot}C_6H_4)_2$]	286·1 *	_690·8_	399·8	—	32·8
(*p*-tolyl)$_2$C:NH	_285·0_	—	398·7	—	—
(*p*-$CF_3{\cdot}C_6H_4)_2$C:NH	_286·3_ *	—	400·1	—	—
π-$C_5H_5Mo(CO)_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$] (A)†	_285·0_	—	400·0	228·4	—
π-$C_5H_5Mo(CO)_2$[(*p*-$CF_3{\cdot}C_6H_4)_2$CNC(*p*-$CF_3{\cdot}C_6H_4)_2$] (A + B)†	286·1 *	_690·8_	401·0	229·3	—
π-$C_5H_5W(CO)_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$] (B)†	_285·0_	—	400·1	—	31·0
π$C_5H_5W(CO)_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$] (A + B)†	_285·0_	—	400·1	—	31·2
(*p*-tolyl)$_2$C:NCHPh$_2$	_285·0_	—	398·8	—	—

* C1*s* (CF_3) at 293·8 eV. † Isomeric forms in the solid state, see discussion. Estimated error in binding energies ± 0·3 eV.

The syntheses of all the complexes, except [π-$C_5H_5W(CO)_2N{:}C(p\text{-}CF_3{\cdot}C_6H_4)_2$], have been described.[11,12] The latter complex was obtained from the reaction of (*p*-$CF_3{\cdot}C_6H_4)_2$C:NLi, previously prepared from *p*-$CF_3{\cdot}C_6H_4Li$ and *p*-$CF_3{\cdot}C_6H_4C{:}N$ in ether solution, with π-$C_5H_5W(CO)_3Cl$ (0·66 g, 1·8 mmol) also in ether solution at ambient temperature. After 4 h the dark green solution was evaporated to dryness, the residue extracted with hexane (6 × 10 ml), and the extract filtered through a ½ inch pad of neutral alumina. Reduction of the volume of the solvent (20 °C *in vacuo*) and cooling to −20 °C yielded three crops of crystals. The first crop of dark green crystals were characterised as π-$C_5H_5W(CO)_2N{:}C(p\text{-}CF_3{\cdot}C_6H_4)_2$ (yield 0·56 g, 45%), m.p. 146—150 °C (decomp.). The second and third crops were shown to be π-$C_5H_5W(CO)_2(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3{\cdot}C_6H_4)_2$ (yield 0·41 g, 22%), m.p. 153—154 °C.

Properties of π-$C_5H_5W(CO)_2N{:}C(p\text{-}CF_3C_6H_4)_2$.—The air-stable, dark green crystals were soluble in all common organic solvents giving green solutions which were air-stable only for short periods: mass spectrum: *m/e* (P^+) 621 (Found: C, 42·30; H, 2·25; N, 2·25. Calc. for $C_{22}H_{13}F_6NO_2W$: C, 42·50; H, 2·10; N, 2·25%); i.r. $\nu_{(CO)}$ in KBr: 1956s, 1869s cm^{-1}; in hexane, 1975s, 1898s cm^{-1}; ^1H and ^{19}F n.m.r. (toluene soln.): τ 4·69 (C_5H_5) relative to $SiMe_4$ (τ = 10) and 62·9 p.p.m. (CF_3) upfield from $CFCl_3$.

RESULTS AND DISCUSSION

Qualitative Discussion.—The complexes studied fall into two groups: methyleneamino-complexes, π-$C_5H_5M(CO)_2N{:}CR_2$, and aza-allyl/allene complexes, π-$C_5H_5M(CO)_2[R_2CNCR_2]$ (M = Mo and W; R = *p*-tolyl and *p*-$CF_3{\cdot}C_6H_4-$). Their experimental binding energies (BE's) and those of free ligand model compounds are in Table 1. An interesting feature of the spectra from molybdenum complexes is the close proximity of the N1*s* and Mo3$p_{3/2}$ levels. The latter core level is less convenient for accurate study than the 3$d_{5/2}$ level because of its greater inherent linewidth; however, the spectra in this region give an immediate picture of the nitrogen and molybdenum BE's and allow relative shifts to be measured without the error imposed by corrections to reference levels. This point is illustrated in Figure 1. It is clear that in going from the methyleneamino-complex to the aza-allyl/allene complex that the increase in N1*s* BE is accompanied by a decrease in the BE of the metal core levels. This suggests that the electron density increases at the metal atom and decreases at the nitrogen of the ligand on replacing the methyleneamino- by the aza-allyl/allene group. In the two complexes shown the π-$C_5H_5Mo(CO)_2$ moiety can be thought of as being bonded to the three-electron donors (*p*-tolyl)$_2$C:N– and (*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$ respectively. The bonding aspects will be discussed in more detail below, but the peak separations show directly that this description must, at least, be a reasonable approximation. The shifts in BE's of the Mo3$p_{3/2}$ level are mirrored by the more accurately measurable Mo3$d_{5/2}$ level quoted in Table 1.

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[10] D. T. Clark and D. Kilcast, *Chem. Comm.*, 1971, 516.

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

[12] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 1535.

It is apparent from the metal and N1*s* BE's that the shifts in going from one complex of Mo to its analogue in the W series are not significantly different. Moreover, the shifts in BE's for each metal in going from π-$C_5H_5M(CO)_2NC$(*p*-tolyl)$_2$ to π-$C_5H_5M(CO)_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$] type complexes are the same (*ca.* 0·6 eV). This result may be expected in view of the fact that the atomic radii of the two metals are very similar.

TABLE 2

W Complexes	W4$f_{7/2}$ BE/eV	ν_{CO}(KBr)/cm^{-1} [a]
π-$C_5H_5W(CO)_2$[NC(*p*-tolyl)$_2$]	31·6	1938, 1838
π-$C_5H_5W(CO)_2$[NC(*p*-CF_3·C_6H_4)$_2$]	32·3	1956, 1869
π-$C_5H_5W(CO)_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$] (B)	31·0	1931, 1830
Mo Complexes	Mo3$d_{5/2}$ BE/eV	
π-$C_5H_5Mo(CO)_2$[NC(*p*-tolyl)$_2$]	229·0	1949, 1855
π-$C_5H_5Mo(CO)_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$]	228·4	1936, 1836
π-$C_5H_5Mo(CO)_2$[(*p*-CF_3·C_6H_4)$_2$CNC(*p*-CF_3·C_6H_4)$_2$] (A + B)	229·3	1958, 1873 [b]

[a] Data from refs. 11, 12. [b] Mean of frequencies from two isomers: 1963, 1880 and 1954, 1866 cm^{-1}.

The long-range effects of changing the *para*-substituents on the aryl groups can be readily seen in both methyleneamino- and aza-allyl/allene complexes. Changing CH_3 to CF_3 would be expected to lower the electron density at nitrogen and the metal, through the powerful electron-withdrawing influence of the *p*-CF_3 group; indeed, the N1*s* BE's in both types of complex are seen to increase by 1 eV while the metal BE's increase significantly also. Such electronic effects in aza-allyl/allene complexes have been inferred from correlations of carbonyl stretching frequencies with the electronic properties of the *para*-substituents as indicated by their Hammett σ-constants.[13] Table 2 collects the metal BE's and solid-state carbonyl stretching frequencies, while Figure 2 correlates these two parameters (using the higher of the two ν_{CO} values). The parallel trends show that the correlation is independent of the metal which is further indication of the very close similarity between complexes of Mo and W. Since both methyleneamino- and aza-allyl/allene complexes are used in this correlation the good fit obtained offers direct evidence for the widely accepted belief that carbonyl groups exert a strong stabilising effect in complexes of metals in low formal oxidation states through dissipation of excess of electron density on the central metal atom. There is no good theoretical reason why such correlations should be linear but since both measurements monitor to a lesser or greater extent the electronic environment of the metal atom a definite trend would be expected.

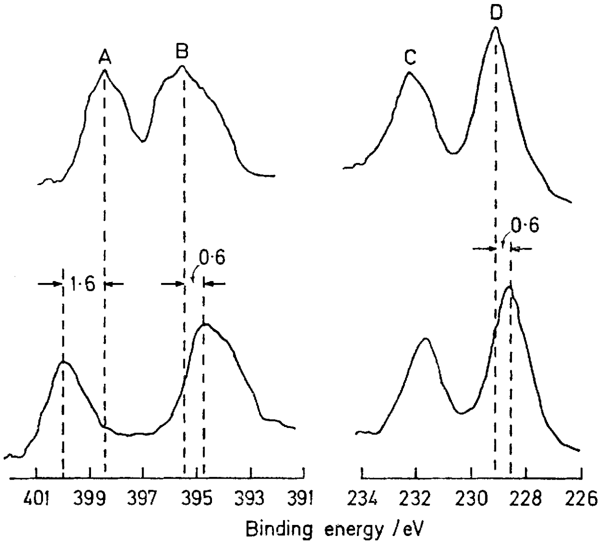

FIGURE 1 E.s.c.a. spectra of π-CpMo(CO)$_2$[NC(*p*-tolyl)$_2$] (upper curves) and π-CpMo(CO)$_2$[(*p*-tolyl)$_2$CNC(*p*-tolyl)$_2$] (lower curves) showing peaks due to A, N1*s*; B, Mo3$p_{3/2}$; C, Mo3$d_{3/2}$; and D, Mo3$d_{5/2}$

Methyleneamino-complexes.—A large variety of data has already been accumulated in order to resolve the question of bonding in complexes involving the methyleneamino-ligand, $R_2C{:}N^-$, which could either act as a one- or three-electron donor (bent or linear M–N–C skeletons respectively) depending on the involvement of

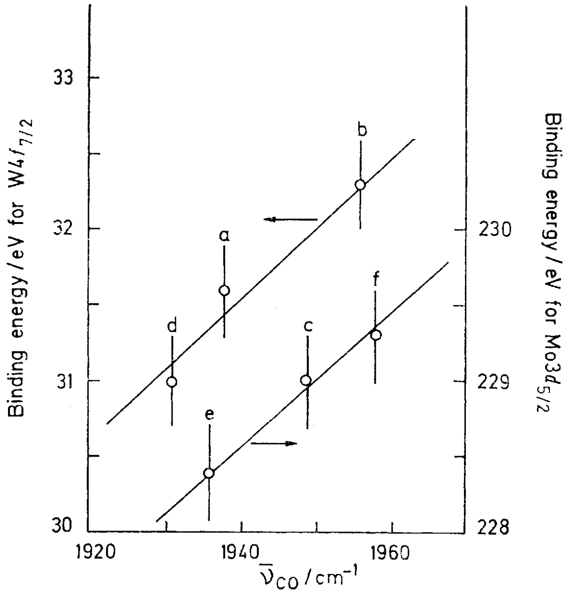

FIGURE 2 Correlation of ν_{CO} and binding energy π-$C_5H_5M(CO)_2N{:}CR_2$: a, M = W, R = *p*-tolyl; b, M = W, R = *p*-CF_3·C_6H_4; and c, M = Mo, R = *p*-tolyl; π-$C_5H_5M(CO)_2R_2CNCR_2$: d, M = W, R = *p*-tolyl; e, M = Mo, R = *p*-tolyl; and f, M = Mo, R = *p*-CF_3·C_6H_4

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[13] H. R. Keable and M. Kilner, unpublished results.

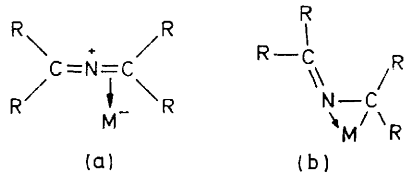
the nitrogen lone pair. Variable-temperature ^1H and ^{19}F n.m.r. spectra for the complexes with R = Bu^t,[14,15] *p*-tolyl,[13] *and* *p*-$CF_3{\cdot}C_6H_4$ [13] respectively (the aryl groups having fairly low steric requirements) strongly suggest a linear M–N–C skeleton. *X*-Ray diffraction data for π-$C_5H_5Mo(CO)_2NCBu^t_2$ [16] showed a virtually linear skeleton and a short M–N bond, possibly arising from considerable multiple bonding, although a model indicated that linearity may be due to steric requirements of the ligand and not solely to electronic effects. C=N stretching frequencies for complexes in which R = Bu^t are not appreciably lowered from those of the free methyleneamine as might be expected if back donation were significant. Methyleneamine-groups bound linearly to the main-group metals and metalloids [17] where $d\pi \longrightarrow \pi^*$ back donation is not possible (*e.g.*, Be, B, Al, or Si) or unlikely (*e.g.*, Ga) show significant increases in ν_{CN} but as the co-ordinating element becomes heavier this increase becomes smaller [18] and the small changes for transition-metal complexes are in keeping with this trend. Hence σ and $p\pi$–$d\pi$ donation processes which tend to increase ν_{CN} may be effectively balanced by $d\pi \longrightarrow \pi^*$ back bonding. In the complexes studied here the C=N frequencies are obscured by ring vibrations of the aryl groups so this information is lacking.

Referring to the relevant figures in Table 1 we see that there is no statistically significant alteration of the N1*s* BE's of the methyleneamines on replacement of the hydrogen by a $M(CO)_2(\pi\text{-}C_5H_5)$ moiety. This indicates that the electron density on nitrogen is virtually unaltered which suggests that either the lone pair is not involved in bonding or that the (σ and π)-donor and π-acceptor tendencies of the ligand are effectively balanced. The fact that long-range electronic effects are efficiently transmitted from *para*-positions on the aryl groups *via* nitrogen and the metal to the carbonyl groups argues the presence of a conjugated π-system and, therefore, favours the latter explanation. It is therefore likely that for all types of R group in $R_2C{:}N$– ligands the M–N–C skeleton will be linear as a result of maximum overlap of the nitrogen lone pair (in a *p* orbital) with suitable metal *d* orbitals. Back donation ($d\pi \longrightarrow \pi^*$) can then increase synergically with this increase in $p\pi$–$d\pi$ bonding.

Aza-allyl/allene Complexes.—The aza-allyl/allene ligand is thought to act as a three-electron donor (thus fulfilling the inert-gas rule for the metal) on the basis of (*a*) the failure to add a further neutral 2-electron donor such as triphenylphosphine or even CO under conditions of high temperature and pressure,[19] and (*b*) the low carbonyl frequencies indicating dissipation of high charge build-up on the metal as described above.

For the complexes studied, π-$C_5H_5M(CO)_2[R_2CNCR_2]$ (M = Mo or W; R = *p*-tolyl or *p*-$CF_3{\cdot}C_6H_4$), two isomers exist in the solid state (forms A and B). The possible nature of these isomers and the isolation of form A (M = Mo, R = *p*-tolyl) (1) and form B (M = W, R = *p*-tolyl) has been discussed.[11] The crystal structure of (1) shows that the ligand adopts the aza-allene bonding mode;[16] the observed molecular geometries [16] and interatomic distances are not inconsistent with either of the extreme bonding modes (Figure 3). The first [Figure 3(a)] involves transfer of an electron to the metal leaving a positively charged ligand which is isoelectronic with the allenes; the ligand then acts as a two electron mono-olefin-type donor resulting in a CNC bond angle less than 180°. The second [Figure 3(b)] would imply bonding of the aza-allene radical, $R_2C{=}N{-}\dot{C}R_2$, *via* a metal–carbon bond and σ-donation of the nitrogen lone pair, resulting in formation of an essentially σ-bonded three-membered ring.

The bonding situation illustrated in Figure 3(a) could be expected to be similar to that found in transition-metal allene complexes involving σ-donation from the ligand and $d\pi \longrightarrow \pi^*$ back donation. Such complexes being considered, the similarity of C–C bond lengths for the 'free' and complexed ligand, and their slight deviation from the normal olefinic C–C distance,[20] indicates that the latter process has little effect on the co-ordinated C–C bond length. The metal–carbon bond distances in such complexes tend to be slightly longer than those in metal alkyls. In the aza-allene complex the co-ordinated C–N bond length is that of a single bond and the Mo–N and Mo–C distances are slightly shorter than single bonds. Back donation appears to play a significant role. This is only to be expected for the postulated positively charged ligand and a parallel could be drawn between this ligand and tetracyanoethylene which, as a poor σ-donor and very strong π-acceptor, displays almost single C–C bond distances in its complexes.[21] The C–N bond lengths also indicate more extensive back donation than in the corresponding methyleneamino-complexes (see above). The flow of electron density to the ligand could balance, if not exceed, initial transfer of an electron to the metal, in view of the reduction of the co-ordinated C–N bond



(a) (b)

FIGURE 3 Bonding modes of the aza-allene group in π-$C_5M_5Mo(CO)_2[(p\text{-tolyl})_2CNC(p\text{-tolyl})_2]$

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[14] M. Kilner and C. Midcalf, *Chem. Comm.*, 1970, 552.

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

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[17] R. Snaith, C. Summerford, K. Wade, and B. K. Wyatt, *J. Chem. Soc.* (*A*), 1970, 2635.

[18] J. B. Farmer and K. Wade, personal communication.

[19] T. Inglis and M. Kilner, unpublished results.

[20] J. G. Hewitt and J. J. De Boer, *J. Chem. Soc.* (*A*), 1971, 817.

[21] C. Parattoni, E. Bombieri, U. Belluco, and W. H. Baddley, *J. Amer. Chem. Soc.*, 1968, **90**, 798.

order to unity. For this bonding mode, therefore, the nitrogen binding energy would not be expected to differ greatly from that of the free ligand while the metal binding energy might compare with that found for the corresponding methyleneamino-complex where donation to and from the metal appear to balance also.

In the other bonding mode the more effective Mo–N bonding would take place with the nitrogen lone pair occupying an orbital of near sp^2 hybridisation, with most of the electron density directed towards the metal. The Mo–N and Mo–C distances may imply a degree of back donation. This may occur for the Mo–N bond by $d\pi \longrightarrow \pi^*$ donation into the orthogonal π^* orbitals of the unco-ordinated C=N system, but for the structure shown in Figure 3(b) there would be no π^* orbital available for back donation on the unco-ordinated carbon atom. A less extreme structure than that shown, in which some π character is given to the co-ordinated C–N bond, must be invoked to fit the observed structural parameters. The net result is still likely to be one in which a build-up of electron density occurs on the metal, at the expense of the nitrogen.

Consider now the BE data in Table 1. The N1*s* BE (400·0 eV) for $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2[(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2]$ is 1·3 eV greater than in $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2\text{NC}(p\text{-tolyl})_2$ and 1·2 eV greater than in $(p\text{-tolyl})_2\text{C=NCHPh}_2$. The latter may be taken as a reasonable model for the free aza-allyl/allene ligand since as far as the N1*s* BE is concerned there is expected to be little difference between $(p\text{-tolyl})_2\text{C=N–CHPh}_2$ and $(p\text{-tolyl})_2\text{C=N–}\dot{\text{C}}\text{Ph}_2$. Such increases in BE indicate a considerable relative reduction of electron density at nitrogen. There is also a significant increase in the metal electron density in going from the methyleneamino- to the aza-allyl/allene complex (0·6 eV decrease in BE). These data suggest that bonding of the aza-allyl/allene group to molybdenum involves a greater degree of electron donation from ligand to metal than is apparent in the analogous methyleneamino-complexes, rather than the predominantly metal–ligand back donation process implied by the structure shown in Figure 3(a). This is good evidence for the direct involvement of the nitrogen lone pair in bonding as described above for a less extreme case of Figure 3(b).

The structure of the 'form B' isomer is unknown, though the similarity of the i.r. spectrum to that of the common type in solution [12] suggests that the ligand may adopt the aza-allylic arrangement. No significant broadening of the N1*s* or Mo3*d* peaks from a sample containing approximately equal quantities of A and B isomers of $\pi\text{-C}_5\text{H}_5\text{W(CO)}_2[(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2]$ with respect to the pure B form was detected so it can be confidently asserted that whatever structure is adopted the electron distribution is essentially the same in both A and B forms.

Similar isomeric forms are thought to exist for the complexes $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_2(p\text{-CF}_3\cdot\text{C}_6\text{H}_4)_2\text{CNC}(p\text{-CF}_3\cdot\text{C}_6\text{H}_4)_2$ (M = Mo or W).[12] The Mo compound contains approximately equal proportions of the two isomers and these cannot be separated by fractional crystallisation. Broadening of the Mo3*p* and 3*d* peaks is significant, whereas the N1*s* peak has the same half-widths as found in all other spectra (1·7—1·8 eV). This may be an artifact due to differential charging effects but this is considered to be very unlikely since the isomers crystallise as an intimate mixture. The difference between the higher-frequency ν_{CO} signals for the two forms is 8 cm^{-1} in this complex compared with only *ca.* 3 cm^{-1} for the complex with *p*-tolyl groups (by analogy with the data from the W complex which has been isolated in both isomeric forms. From the correlation of BE with ν_{CO} (Figure 2) it may be deduced that a BE difference large enough to give detectable line broadening would only be expected for the case where $\Delta\nu_{CO} > 8$ cm^{-1}.

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