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Indenylmethyl-molybdenum and -tungsten compounds containing isocyanide ligands. Formation and study of isomeric η^2-iminoacyls and η^3-1-azaallyls†

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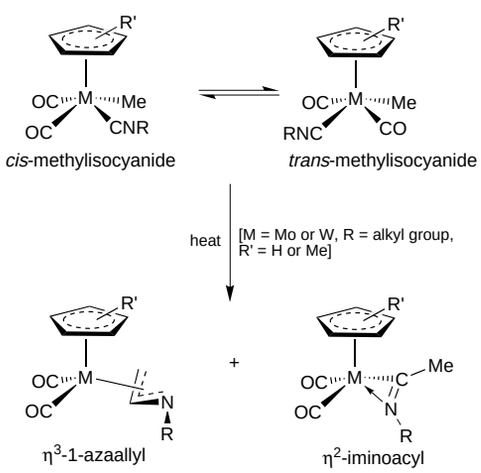
Mild thermolysis of benzene solutions of the methylisocyanides $[M(\eta^5\text{-}C_9H_7)Me(CO)_2(CNBu^t)]$ (M = Mo or W) cleanly afforded mixtures of isomeric dihapto-iminoacyls $[M(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ and trihapto-azaallyls $[M(\eta^5\text{-}C_9H_7)\{\eta^3\text{-}H_2CC(H)NBu^t\}(CO)_2]$. Compared to such transformations in cyclopentadienyl- or methyl-substituted cyclopentadienyl-containing analogues investigated previously, a significantly greater proportion of the dihapto-iminoacyl products are generated. Solution NMR studies of the products demonstrated that both types of complex are fluxional at room temperature, for the η^2-iminoacyls the fluxionality being conveniently envisaged as a rotation of the bound nitrogen-containing fragment about an axis passing through the metal atom and the ligand centroid. In the case of the azaallyl products the temporary attainment of a planar metallaazacyclobutenyl structure is invoked to explain the dynamic behaviour. Two compounds, $[W(\eta^5\text{-}C_9H_7)Me(CO)_2(CNBu^t)]$ and $[W(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ have been characterized in the solid state by single-crystal X-ray diffraction.

Among our research interests is the study of the commercially important insertion of electronically unsaturated ligands like carbonyl and isocyanide functionalities into metal–carbon σ bonds to produce acyl and iminoacyl ligand fragments.[1] As a continuation of this work we recently reported the preparation and characterization of a range of molybdenum and tungsten cyclopentadienyl (cp = η^5-C_5H_5) and methyl-substituted cyclopentadienyl (η^5-C_5H_4Me, η^5-C_5Me_5) methylisocyanide complexes of general formula $[M(\eta^5\text{-}C_5H_{5-n}R_n)Me(CO)_2(CNR)]$ (R = alkyl group). Their transformation to the isomeric η^2-iminoacyl $[M(\eta^5\text{-}C_5H_{5-n}R_n)\{\eta^2\text{-}C(=NR)Me\}(CO)_2]$ and η^3-1-azaallyl $[M(\eta^5\text{-}C_5H_{5-n}R_n)\{\eta^3\text{-}H_2CC(H)NR\}(CO)_2]$ derivatives during clean, intramolecular rearrangements was described (Scheme 1).[2] The η^2-iminoacyls are clearly the result of classic migratory insertion reactions whilst the η^3-1-azaallyls have been proposed to derive from a metal-mediated 1,2 shift of H within the bound iminoacyl fragment.[3] Interestingly, it was found that the relative proportion of η^2-iminoacyl and η^3-1-azaallyl products generated during the thermally induced transformation of methylisocyanides of this type shows a strong dependence upon the choice of metal atom (M = Mo or W), isocyanide alkyl substituent R (Me, Et, Pr^i or Bu^t), and even the reaction solvent (those solvents having good donor abilities tend to favour η^2-iminoacyl production).[2] In some of the cases studied, sensitivity of the product ratio [η^2-iminoacyl]:[η^3-1-azaallyl] to the nature of the cyclopentadienyl ring was observed. Methylisocyanides bearing the bulkier and more electron-releasing pentamethylcyclopentadienyl ligand tended to provide a greater proportion of the η^2-iminoacyl products and correspondingly less of the alternative η^3-1-azaallyls, relative to the unsubstituted cyclopentadienyl cases.[2b]

Herein we describe a study of related η^5-indenyl-containing derivatives, this ligand providing a similar steric environment to the cyclopentadienyl-containing compounds studied before, but having markedly different electronic properties.[4] We detail the syntheses and characterization of indenyl-containing methylisocyanides of Mo and W and also the investigation of the products of their thermolyses. Variable-temperature NMR studies provide information regarding the fluxional behaviour displayed by these complexes in solution. Solid-state characterization by single-crystal X-ray diffraction studies of two derivatives is also presented.

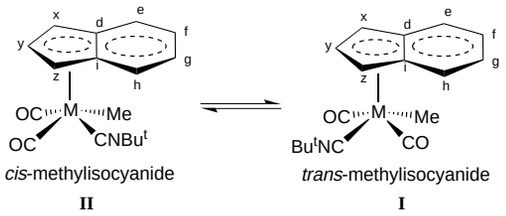


Scheme 1 Thermal transformation of $[M(\eta^5\text{-}C_5H_{5-n}R'_n)(CH_3)(CO_2)(CNR)]$ complexes

Results and Discussion

By a procedure analogous to that previously described[2] for the preparation of $C_5H_{5-n}R_n$-containing compounds of this type (η^5-C_5H_5, C_5H_4Me, C_5Me_5), the low-temperature addition of MeI to tetrahydrofuran (thf) solutions of the pale yellow metalates $Na[M(\eta^5\text{-}C_9H_7)(CO)_2(CNBu^t)]^-$ (M = Mo or W) results in methylation exclusively at the metal centre to generate the

† In memory of Professor G. Wilkinson who led so many of us into Organometallic Chemistry.



cis-methylisocyanide **II** ⇌ *trans*-methylisocyanide **I**

methylisocyanides $[M(\eta^5\text{-}C_9H_7)Me(CO)_2(CNBu^t)]$ (M = Mo **1** or W **2**) in essentially quantitative yields. The successful isolation of pure **1** and **2** required the evaporation of the thf reaction solvent and subsequent extraction into light petroleum to be performed at or below room temperature, the complexes crystallizing as orange-red and yellow solids respectively from that solvent at −30 °C.

Compounds **1** and **2** are readily soluble in all common organic solvents, existing in solution as a mixture of *cis* and *trans* isomers (Scheme 1). In the NMR spectra of these compounds the M–Me group provides resonances most diagnostic of such methylisocyanides,[2,3] originating high-field signals in the range δ −0.3 to 0.3 (^{1}H) and δ −25 to −8 (^{13}C). The lower symmetry of the $\eta^5\text{-}C_9H_7$ ligand compared to $\eta^5\text{-}C_5R_5$ provides a means to distinguish readily between the ^{1}H NMR resonances of the two isomers. Thus, whilst the signals assigned to the protons of the C_6 rings of both isomers of **2** give a series of undistinguishable superimposed multiplets between δ 6.60 and 7.00 in C_6D_6 solvent at room temperature, those resonances assigned to the C_5 rings are partially resolved. Whereas H_x and H_z are chemically equivalent in the *trans* isomer (structure **I**) and as such result in a doublet at δ 5.22 (^3J = 2.9 Hz), these same protons in the *cis* isomer (structure **II**) are inequivalent, giving rise to two broadened multiplets at δ 5.31 and 5.35. From these observations it was also clear that the *cis* isomer predominates in solution, the ratio [*cis*]:[*trans*] being equal to 3.9:1, determined by integration of the appropriate *tert*-butyl resonances. Similar observations were made in the case of **1**, the corresponding ratio [*cis*]:[*trans*] being 3.4:1 for this complex.

In its infrared spectrum (Nujol mull) compound **1** displays strong CO stretching absorptions at 1852 and 1933 cm^{-1}, the approximate equivalence of the band intensities being indicative of the predominance of the *cis* isomer in the solid state.

Monocrystals of compound **2** were grown from light petroleum at −30 °C, enabling the crystal structure of the complex to be determined. A representative ORTEP[5] plot of the structure of **2** is shown in Fig. 1 and key bond distances and angles are presented in Table 1. As anticipated from the IR data, **2** crystallizes with the CO ligands mutually *cis*, representing two of the four legs of the ubiquitous piano-stool geometry. The indenyl ligand is bound to the metal atom through all five members of the C_5 ring, but the bonds to C(1), C(4) and C(5) (*ca.* 2.32 Å, average) are shorter by about 0.2 Å than those to the bridgehead carbon atoms C(2) and C(3) (2.50 Å). This translates into the existence of a ground-state slip distortion[6a] of the indenyl ligand in the direction of C(5), that is towards an η^3-allylic bonding mode. Similar distortions have been observed in other indenyl metal complexes.[6b,c] In accord with these literature reports,[6b] the ligands of greater *trans* influence (the carbonyls) adopt a conformation placing them *trans* with respect to the benzenoid ring. This phenomenon has been observed in the past and was explained as being due to a greater recovery of resonance energy in the benzenoid ring when such ligands are *trans* to the bridgehead carbon atoms. The metal carbonyl groups are linear and have the usual bond lengths, W–C (average) 2.00(2) and C–O (average) 1.22(3) Å. In addition the isocyanide ligand can be defined as linear and the W–Me distance of 2.26(2) Å compares well with that found in other methyltungsten(II) complexes, *e.g.* 2.29(2) Å in $[WMe(acac)(CO)_2(PMe_3)_2]$ (acac = acetylacetonate).[7]

The ^{13}C-{^{1}H} NMR data for compound **2** are consistent with

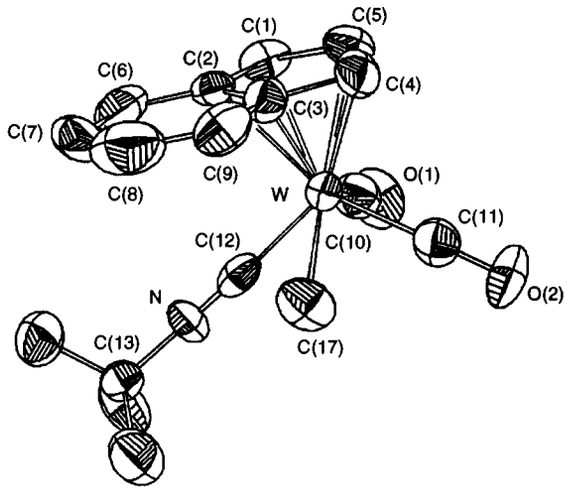


Fig. 1 Molecular structure of complex **2**

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

W–C(1)	2.34(2)	C(2)–C(6)	1.45(2)
W–C(2)	2.52(1)	C(3)–C(4)	1.50(3)
W–C(3)	2.50(2)	C(3)–C(9)	1.40(3)
W–C(4)	2.33(2)	C(4)–C(5)	1.39(3)
W–C(5)	2.30(2)	C(6)–C(7)	1.41(4)
W–C(10)	2.00(2)	C(7)–C(8)	1.35(4)
W–C(11)	2.00(2)	C(8)–C(9)	1.36(3)
W–C(12)	2.04(2)	C(10)–O(1)	1.18(3)
W–C(17)	2.26(2)	C(11)–O(2)	1.26(2)
C(1)–C(2)	1.37(2)	C(12)–N	1.18(2)
C(1)–C(5)	1.44(3)	C(13)–N	1.46(2)
C(2)–C(3)	1.47(2)		
C(17)–W–C(12)	70.2(7)	C(10)–W–C(11)	76.8(8)
C(17)–W–C(11)	76.3(8)	W–C(10)–O(1)	177(2)
C(17)–W–C(10)	129.6(8)	W–C(11)–O(2)	179(1)
C(11)–W–C(12)	11.8(7)	W–C(12)–N	175(1)
C(10)–W–C(12)	81.6(8)	C(12)–N–C(13)	166(2)

the solid-state structure obtained by X-ray methods and indicate, moreover, that the slip distortion of the co-ordinated indenyl ligand persists in solution. Baker and Tulip[6c] have calculated $\Delta\delta(C) = \delta[C(\eta\text{-indenyl})] - \delta[C(\text{indenylsodium})]$ for a number of d^6 and d^8 complexes and have found that the Δδ(C) for the bridgehead carbons C(2) and C(3) (or C_d and C_i in structures **I** and **II**) exhibit a good correlation with the hapticity of the indenyl ligand. For **2** $\Delta\delta[C_{d,i}]$ amounts to *ca.* −20 ppm. Following their conclusions, the existence of a distorted η^5-indenyl ring can be inferred.

As anticipated considering our findings in the study of related cyclopentadienyl-containing compounds,[2] the mild thermolysis (70–80 °C) of benzene solutions of **1** and **2** resulted in clean, irreversible transformations to mixtures of η^2-iminoacyls $[M(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ (M = Mo **3** or W **4**) and η^3-1-azaallyls $[M(\eta^5\text{-}C_9H_7)\{\eta^3\text{-}H_2CC(H)NBu^t\}(CO)_2]$ (M = Mo **5** or W **6**) as shown in Scheme 1. Interestingly, the product distribution [iminoacyl]:[azaallyl] was found to be equal to *ca.* 8:1 in the case of M = Mo and *ca.* 2:1 in the tungsten system. These results contrast sharply with those obtained during the study of similar cyclopentadienyl-containing complexes $[M(\eta^5\text{-}C_5R_5)(Me)(CO)_2(CNBu^t)]$ (M = Mo or W, R = H or Me) for which the corresponding ratios are all less than 0.1:1.[2] The precise explanation why the indenyl ligand should so favour iminoacyl formation in these reactions is unclear at this time; further study of the detailed mechanisms of reaction will probably aid the understanding of this indenyl effect.[8]

Monocrystals of compound **4** suitable for an X-ray diffrac-

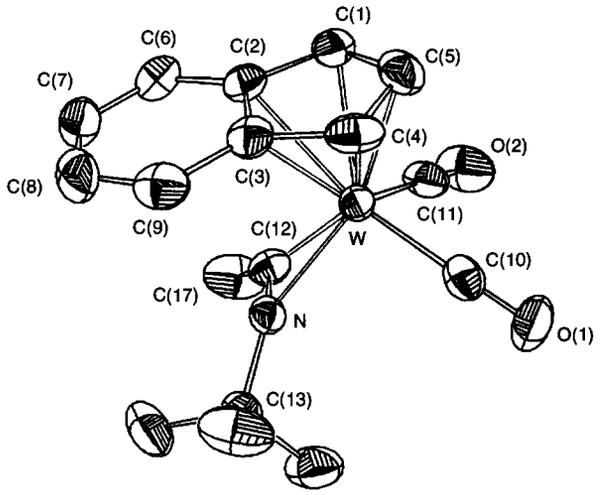


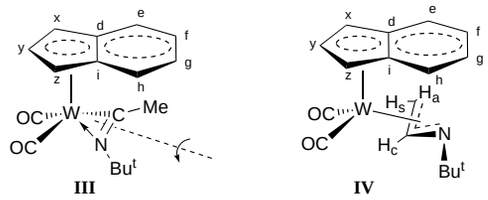
Fig. 2 Crystal structure and atom-labelling scheme for complex **4**

Table 2 Selected bond lengths (Å) and angles (°) for complex **4**

W–C(1)	2.310(7)	C(2)–C(6)	1.44(1)
W–C(2)	2.443(7)	C(3)–C(4)	1.46(1)
W–C(3)	2.481(7)	C(3)–C(9)	1.43(1)
W–C(4)	2.356(8)	C(4)–C(5)	1.40(1)
W–C(5)	2.318(8)	C(6)–C(7)	1.36(1)
W–C(10)	1.917(7)	C(7)–C(8)	1.42(1)
W–C(11)	1.928(8)	C(8)–C(9)	1.34(1)
W–C(12)	2.097(7)	C(10)–O(1)	1.171(9)
W–N	2.144(5)	C(11)–O(2)	1.216(1)
C(1)–C(2)	1.414(9)	C(12)–C(17)	1.49(1)
C(1)–C(5)	1.44(1)	C(12)–N	1.239(8)
C(2)–C(3)	1.426(9)	C(13)-N	1.494(8)
C(12)–W–N	33.9(2)	W–C(10)–O(1)	178.8(6)
C(11)–W–N	114.3(3)	W–C(11)–O(2)	178.2(7)
C(11)–W–C(12)	88.0(3)	W–C(12)–N	75.1(4)
C(10)–W–N	93.9(3)	W–C(12)–C(17)	151.3(6)
C(10)–W–C(12)	109.4(3)	C(17)–C(12)–N	133.0(7)
C(10)–W–C(11)	76.7(3)	C(12)–N–C(13)	136.4(6)
W–N–C(12)	71.0(4)	W–N-C(13)	166(2)

tion study were grown from light petroleum solution at −30 °C; the molecular structure is presented in Fig. 2 as an ORTEP plot and important bond distances and angles are collected in Table 2. As can be observed, complex **4** adopts a conformation in which, once again, the two carbonyls are *trans* to the benzene moiety of the indenyl ligand. The tungsten carbonyls show bond lengths and angles quite similar to those for complex **2** and merit no further discussion. With respect to the iminoacyl ligand it is clearly in the dihapto co-ordination mode[9] with W–C(12) and W–N distances of 2.097(7) and 2.144(5) Å respectively, which compare well with other Group 6 η^2-iminoacyl derivatives.[10] Also, and as first pointed out by Adams and Chodosh[11a] the C(12)–N bond [1.239(8) Å] is shorter than expected for a normal C=N double bond (1.29–1.31 Å), although larger than C≡N bond distances (*ca.* 1.16 Å). This is now recognized as a quite general phenomenon[12] that has been observed even in nickel(II) η^2-iminoacyls.[13] A slip distortion of the co-ordinated indenyl ligand, similar to that previously discussed for **2**, is also apparent in this compound. Thus the bonds from W to C(1), C(4) and C(5) average 2.33 Å, while those to C(2) and C(3) are 0.13 Å longer (2.46 Å, average). This distortion seems to be maintained in solution, as indicated by the observation of the C_d and C_i resonances at δ 113.8 and 119.2, respectively. Since the corresponding signal of indenylsodium has a chemical shift of δ 130.7, $\Delta\delta[C_{d,i}]$ for **4** is *ca.* 14 ppm.[6c]

The NMR resonances of the iminoacyl ligand are unexceptional, being readily assigned by reference to other



related compounds that possess cyclopentadienyl ligands or substituted derivatives thereof,[2,3,11,14,15] and as such they do not merit further comment. The ^{1}H NMR signals due to the indenyl ligand are more interesting; in C_6D_6 solvent at room temperature they consist of a series of multiplets between δ 5 and 7. The four protons of the benzenoid ring give rise (to a first approximation) to doublets (H_e and H_h) or triplets (H_f and H_g), H_x and H_z of the five-membered ring are manifested as two multiplets, whereas H_y gives a triplet centred at *ca.* δ 5. Spin-saturation transfer and NOEDIFF experiments, to be discussed below, are suggestive of a fluxional process that equilibrates the two halves of the indenyl ligand, which a rigid η^2-iminoacyl linkage would, otherwise, render inequivalent. In a formal sense, this process involves rotation of the co-ordinated η^2-iminoacyl and in complexes with other co-ordination environments accounts for the rearrangement of the η^2-iminoacyl (or -acyl) moiety from the 'X-outside' (X = N or O) to the 'X-inside' isomers.[15a] Hoffmann and co-workers[15b] have suggested that the mechanism of the η^2-acyl isomerization involves dissociation of the oxygen atom, with formation of an η^1-acyl intermediate, followed by rotation and subsequent return to the η^2 binding mode. A similar proposal has been advanced to explain the isomerization of a thermodynamically unstable η^2-iminoacyl complex of Zr.[15c] Notwithstanding this, the fluxional behaviour of η^2-iminoacyls is commonly attributed to a rotation of the η^2-iminoacyl ligand (about an axis connecting the midpoint of the C=N double bond and the metal centre), as represented in structure **III** for the tungsten complex $[W(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ **4**. This is more in agreement with the characteristic strength of metal–η^2-iminoacyl linkages[2] and it would be additionally sustained in our case by the observation that the dynamic behaviour registered for **4** does not depend upon the donicity of the NMR solvent employed. Such a fluxional process was first described by Adams and Chodosh[11a] during a variable-temperature NMR study of the related methylcyclopentadienyl complex $[Mo(\eta^5\text{-}C_5H_4Me)\{\eta^2\text{-}C(=NMe)Me\}(CO)_2]$ and later observed by other workers.[15d]

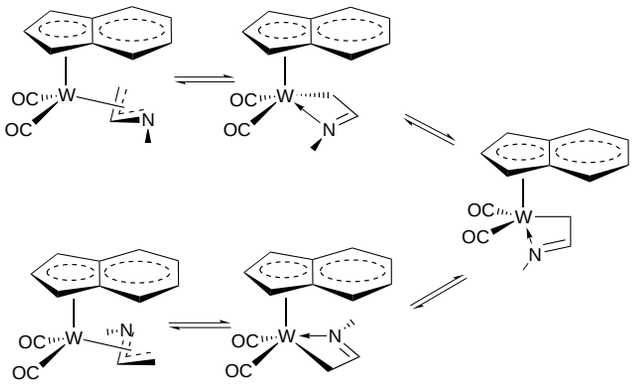
In accord with Adams's findings, the rotation of the iminoacyl ligands in compounds **3** and **4** was found to be slow on the NMR time-scale at room temperature, such that both magnetic environments of the CO and indenyl ligand nuclei may be distinguished readily. In the case of **4** this situation is apparent from the observation of distinct resonances in the ^{1}H NMR spectrum for all seven indenyl protons, the fluxionality being evidenced by spin-saturation transfer between H_x/H_z, H_e/H_h and H_f/H_g upon low-power irradiation of one member of each pair. Furthermore, saturation of the *tert*-butyl singlet in a NOEDIFF experiment at room temperature showed the existence of a significant NOE between the *tert*-butyl protons and H_e/H_h of the benzenoid ring. The fact that both indenyl protons experience a similar NOE under these conditions constitutes additional evidence for the fluxional process described. Conducting the NOEDIFF experiment at −60 °C (at which temperature iminoacyl ligand rotation is slow on the irradiation experiment time-scale) in CD_3COCD_3 as before led to enhancement at only one of the two C_6 protons positioned α to the bridgehead, that lying to higher field (δ 7.31) assigned H_h. This information together with that obtained from routine two-dimensional homo- and hetero-nuclear correlation spectroscopy experiments[4d] permitted the assignment of both the ^{1}H and ^{13}C NMR spectra of **4** and (by analogy) **3** to be made (see Experimental section).

The other product which derives from the thermolysis of compound **2** in benzene is the η^3-1-azaallyl $[W(\eta^5\text{-}C_9H_7)\{\eta^3\text{-}H_2CC(H)NBu^t\}(CO)_2]$ **6**. In contrast to the isomeric methylisocyanide and η^2-iminoacyl compounds this brown-yellow crystalline solid is rather insensitive to air and moisture, however like them it displays high solubility in all common organic solvents. In its infra-red spectrum **6** exhibits carbonyl stretching absorptions at 1867 and 1950 cm^{-1}, some 30 cm^{-1} to higher frequency than the corresponding CO modes in the η^5-C_5H_5-containing analogue, and 20 cm^{-1} higher than the corresponding pentamethylcyclopentadienyl compound.[2] These data imply a reduction in M–CO back donation in this indenyl derivative compared to the cyclopentadienyl-containing compounds.

In the ^{1}H NMR spectrum of compound **6** in C_6D_6 the η^3-1-azaallyl ligand is evidenced by a characteristic pattern of three doublets of doublets centred at δ −0.18, 3.31 and 5.05, assigned respectively to H_a, H_s and H_c of the azaallyl fragment (structure **IV**). The high upfield shift of H_a compared to other non-indenyl-containing η^3-1-azaallyls suggests that H_a experiences an important shielding interaction with the magnetically anisotropic benzenoid ring, as reported previously in studies of η^3-allyls.[6] Since only resonances for one of the four possible conformers were detected, the high upfield shift of H_a implies an *endo* orientation of the azaallyl fragment in **6**. Additionally, ^{1}H NMR experiments established that the *tert*-butyl group is *syn* to the central allylic proton H_c, thus saturation of the *tert*-butyl singlet resulted in enhancement of the resonance assigned to H_c but *not* in that of H_a. From the data obtained it is quite clear that the azaallyl group, as is the iminoacyl ligand in structure **III**, is maintained most of the time facing the benzenoid ring, *i.e.* in the conformation found in the solid state, although this does not require a locked indenyl ligand. The assignment of a *syn*, *endo* conformation to **6** is in accord with all the other mononuclear η^3-1-azaallyls of this general class that have been fully characterized either in a solution or the solid state.[16] In the first such study Green *et al.*[16a] prepared the complex $[Mo(\eta^5\text{-}C_5H_5)\{\eta^3\text{-}H_2CC(R')NH\}(CO)_2]$ (R′ = Ph or C_6H_4Me-4) from the reaction of aziridines with the unsaturated bimetallic molybdenum complex $[\{Mo(cp)(CO)_2\}_2]$. Only *endo* conformations were observed, due, it was suggested, to adverse steric interactions between the hydrocarbyl substituent R′ and the cp ring which were proposed to destabilize a potential *exo* conformation. However, all subsequent studies of complexes of the class $[M(\eta^5\text{-}C_5H_{5-n}R_n)(\eta^3\text{-1-azaallyl})(CO)_2]$ (M = Mo or W) have found an *endo* isomer to be the exclusive product both in solution and in the solid state.[2,3,16]

A fluxional process seemingly related to that of the η^2-iminoacyl complexes **3** and **4** was detected during the solution study of **6**, thus irradiation of H_x caused a simultaneous reduction in the intensity of the resonance assigned to H_z. This spin-saturation transfer was observed to be of the same order of magnitude in **6** than in the isomeric η^2-iminoacyl complex **4**, a result which may be taken to indicate that the η^3-1-azaallyl fragment undergoes dynamic behaviour similar in nature to that of the η^2-iminoacyl ligand in **3** and **4**. However, in the case of **6**, such a rotation must be less facile, as a consequence of the azaallyl fragment's occupancy of more space at the metal co-ordination sphere than its iminoacyl counterpart and more important it cannot explain the observed $H_x \leftrightarrow H_z$ interconversion.

A possible explanation for our observations invokes the intermediacy of a planar, metallaazacyclobutenyl species (Scheme 2).[17] Such a unit could readily undergo a pseudo-rotation,[18] before collapsing back to the *syn*, *endo*, η^3-allylic bonding mode. This mechanism (or a variation thereof) appears to be a more plausible rationale for the room-temperature fluxional behaviour than the alternative temporary dissociation of a ligand terminus, followed by a rotation of the then η^1-co-ordinated ligand. This is because such a process would involve the generation of an electron-deficient intermediate, likely a higher-energy process than the simple mechanism mentioned previously. Moreover, and as discussed for the η^2-iminoacyl **4**, the molecular fluxionality described for this complex showed no apparent dependence upon the donor ability of the NMR solvent employed, the same basic features being observed in CD_3COCD_3 as in C_6D_6.



Scheme 2 Proposed fluxional mechanism for complex **6**

Irrespective of the mechanism in operation, the implication is that the compound has an important thermodynamic stabilization of the *syn*, *endo* conformer over the other three possible conformations. That the energy difference between this structure and its alternatives should be so great as to preclude detection of the latter was surprising. In the light of our recent work it now appears improbable that the reason for exclusive adoption of the *syn*, *endo* conformation by these η^3-1-azaallyls should be purely steric in origin. Indeed, even those η^3-1-azaallyls bearing less bulky methyl or ethyl substituents bound to nitrogen adopt only an *endo* orientation.[2,3,16] A theoretical appraisal of the bonding in $[M(cp)(\eta^3\text{-allyl})(CO)_2]$ complexes traced the observed predominance for an *endo* conformation to electronic effects between the allyl ligand and the $M(cp)(CO)_2$ fragment.[19] Nevertheless, the free-energy differences between the *endo* and *exo* orientations of η^3-allyl fragments were calculated to be small, such that both conformers are normally detected in solution.[20] Noteworthy in the context of the present study is the clear thermodynamic preference for the *syn*, *exo* conformer in the molybdenum η^5-indenyl complex $[Mo(\eta^3\text{-}C_9H_7)\{\eta^3\text{-}H_2CC(H)CHMe\}(CO)_2]$.[6b] Bearing in mind the similarities between this type of complex and **6**, the observation of an *exo* conformer of **6** might reasonably have been predicted, however the results described herein show this not to be the case. It seems probable that the azaallyl orbital described as containing the formally non-bonding nitrogen 'lone pair' is playing a significant role in determining the azaallyl conformational stability, since its presence is the only possible cause for the effect so far not examined.[2,3,16] A recent study of the electronic structures of these complexes by photoelectron spectroscopy[21] revealed that this orbital does *not* display ionization character typical of a non-bonding orbital. Molecular orbital calculations supported the assertion, finding a significant repulsive (filled–filled) interaction between the azaallyl fragment nitrogen lone pair and a metal d orbital. Taking this into account we speculate that the adoption of an *endo* conformation in these η^3-1-azaallyls may be a manifestation of this electronic interaction.

In conclusion, the preparation of two indenyl-containing methylisocyanides $[M(\eta^5\text{-}C_9H_7)Me(CO)_2(CNBu^t)]$ (M = Mo **1** or W **2**) has been described. As anticipated considering the literature precedent, when subject to mild thermolysis in benzene they have been shown to transform into mixtures of isomeric η^2-iminoacyls $[M(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ (M = Mo **3** or W **4**) and η^3-1-azaallyls $[M(\eta^5\text{-}C_9H_7)\{\eta^3\text{-}H_2CC(H)NBu^t\}(CO)_2]$ (M = Mo **5** or W **6**), the latter adopting exclusively a *syn*, *endo* conformation. However, in contrast to previous findings describing such transformations in their

cyclopentadienyl-containing analogues,[2] the presence of the indenyl ligand significantly enhances the relative proportion of the η^2-iminoacyl products obtained at the expense of the alternative η^3-1-azaallyls. This is attributed to an electronic effect exerted by the indenyl ligand at the metal centre, although the precise nature of this interaction is unknown. A further contribution from these laboratories will contain a detailed kinetic study of these and related reactions in addition to a discussion of the intimate mechanisms of transformation.[8]

Experimental

All manipulations were carried out under dry, oxygen-free dinitrogen using standard vacuum-line techniques[22] or in a Vacuum Atmospheres dry-box. Solvents were refluxed over appropriate drying agents under a dinitrogen atmosphere and distilled immediately prior to their use. The light petroleum had a b.p. 40–60 °C. The alumina used for chromatographic separation was Merck 70–230 mesh, oven dried for 24 h and cooled under dynamic vacuum overnight prior to use. The cryostat employed in the low-temperature chromatography separation was a Haake model KT90 which circulated ethanol through jacketed glassware.

Elemental analyses were performed by the Analytical Service of the University of Sevilla. The NMR spectra were recorded on Bruker AMX-500, AMX-300 and Varian XL-200 instruments and referenced to external $SiMe_4$ (δ 0) using the residual protio peaks as internal standards (^{1}H experiments) or the characteristic resonances of the solvent nuclei (^{13}C). The assignments given in subscripts refer to the molecules as represented in structures **I**–**IV**. Infrared spectra were obtained as Nujol mulls either on Perkin-Elmer 577 or 684 spectrometers. The precursor materials $[M(\eta^5\text{-}C_9H_7)I(CO)_2(CNBu^t)]$ (M = Mo or W) were prepared following a methodology entirely analogous to that described in the literature for the preparation of similar cyclopentadienyl-containing complexes,[2b,23] and characterized by comparison of their NMR spectra with those published.[15,23]

Preparation of complexes

$[Mo(\eta^5\text{-}C_9H_7)Me(CO)_2(CNBu^t)]$ 1. A red thf solution (*ca.* 100 cm^3) of $[Mo(\eta^5\text{-}C_9H_7)I(CO)_2(CNBu^t)]$ (5.0 g, 10.5 mmol) was transferred at room temperature onto a mercury amalgam containing sodium (0.5 g, 21.7 mmol, excess). Stirring was continued for 2 h, during which time the solution lightened to a transparent orange; a pale suspended solid also could be observed. The orange solution was later transferred to a clean vessel and cooled to −78 °C. Methyl iodide (1.0 cm^3, 15.5 mmol, excess) was added to the vigorously stirred cold solution *via* syringe; no obvious signs of reaction were apparent following the addition. The flask was allowed to warm slowly to room temperature, at which point the solvent was evaporated to dryness *in vacuo* affording an oily red solid. The product was extracted into light petroleum (2 × 40 cm^3), filtered and reduced in volume to 30 cm^3 before being left to crystallize overnight at −30 °C. Only one crop of analytically pure orange-red crystals was obtained, the extreme solubility of the material, in addition to the suspected presence of an oily impurity, precluding further crystallizations. Compound **1** is a low-melting solid prone to transform into mixtures of η^2-iminoacyl and η^3-1-azaallyl in the solid state at room temperature over the course of a few hours, thus invalidating any elemental analysis. Yield: 1.65 g (43%). IR (Nujol mull, cm^{-1}): 2110m (ν_{CN}); 1950 (sh), 1933s, 1867m and 1852s (ν_{CO}). ^{1}H NMR (C_6D_6): δ −0.20 (s, 3 H, $MoMe_{cis}$), 0.21 (s, 3 H, $MoMe_{trans}$), 0.79 (s, 9 H, $CMe_{3\ cis}$), 0.97 (s, 9 H, $CMe_{3\ trans}$), 4.91 (overlapping triplets, H_y, both isomers, ^3J = 2.9 Hz), 5.24, 5.38 (overlapping multiplets, H_x and H_z of both isomers) and 6.70–7.10 (overlapping multiplets, $H_{e–h}$, both isomers). ^{13}C-{^{1}H} NMR (C_6D_6): δ −12.1 ($MoMe_{trans}$), −8.0 ($MoMe_{cis}$), 29.1 ($CMe_{3\ trans}$), 29.7 ($CMe_{3\ cis}$), 55.5 ($CMe_{3\ cis}$), 77.8, 79.5 (C_x and C_z, *cis* isomer), 80.3 (C_x and C_z, *trans* isomer), 89.1 (C_y, *cis* isomer), 90.4 (C_y, *trans* isomer), 109.8, 113.1 (C_d and C_i, *cis* isomer), 122.0–126.0 (overlapping signals, $C_{e–h}$, both isomers), 230.9 (2 CO), 238.4, 250.8 (CO). Isocyanide C=N and CMe_3, C_d and C_i of *trans* isomer not observed. Ratio of isomers [*cis*] : [*trans*] = 3.4 : 1.

$[W(\eta^5\text{-}C_9H_7)Me(CO)_2(CNBu^t)]$ 2. This complex was prepared by a method analogous to that described above for **1**. The compound $[W(\eta^5\text{-}C_9H_7)I(CO)_2(CNBu^t)]$ (3.2 g, 5.6 mmol) was dissolved in thf (*ca.* 50 cm^3) and reduced by sodium (0.3 g, 13.0 mmol, excess) in a mercury amalgam. Subsequent reaction with methyl iodide (0.6 cm^3, 9.3 mmol, excess), and work-up as above furnished **2** as yellow needles. Yield: 1.83 g (72%) (Found: C, 44.99; H, 4.46; N, 3.08. $C_{17}H_{19}NO_2W$ requires C, 45.03; H, 4.19; N, 3.09%). IR (Nujol mull, cm^{-1}): 2108m (ν_{CN}), 1935 (sh), 1927s, 1932m (ν_{CO}). ^{1}H NMR (C_6D_6): δ −0.09 (s, 3 H, WMe_{cis}), 0.33 (s, 3 H, WMe_{trans}), 0.83 (s, 9 H, $CMe_{3\ cis}$), 1.03 (s, 9 H, $CMe_{3\ trans}$), 4.88 (overlapping triplets, H_y, both isomers, ^3J = 2.8), 5.22 (d, H_x/H_z, *trans* isomer, ^3J = 2.9 Hz), 5.31, 5.35 (br m, H_x/H_z, *cis* isomer) and 6.60–7.00 (overlapping multiplets, $H_{e–h}$, both isomers). ^{13}C-{^{1}H} NMR (C_6D_6): δ −24.1 (WMe_{trans}), −20.4 (WMe_{cis}), 29.8 ($CMe_{3\ trans}$), 30.6 ($CMe_{3\ cis}$), 56.5 ($CMe_{3\ cis}$), 75.9, 77.3 (C_x and C_z, *cis* isomer), 78.3 (C_x and C_z, *trans* isomer), 87.5 (C_y, *cis* isomer) 88.7 (C_y, *trans* isomer), 109.4, 113.3 (C_d and C_i, *cis* isomer), 124.0–126.0 (overlapping signals, $C_{e–h}$, both isomers), 221.6 (2 CO), 229.6, 240.8 (CO). Isocyanide C=N and CMe_3, C_d and C_i of *trans* isomer not observed. Ratio of isomers [*cis*] : [*trans*] = 3.9 : 1.

$[Mo(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ 3. A solution of compound **1** (1.1 g, 3.0 mmol) in benzene (*ca.* 30 cm^3) was heated in a sealed Young's ampoule at 70 °C with stirring for 2 h. During that time the originally orange-red solution became an intense, opaque red. The solvent was evaporated completely *in vacuo* giving a dark red gum. Extraction into light petroleum, followed by concentration and crystallization at −30 °C, resulted in the deposition of dark red needles of **3**. Yield: 0.75 g (68%) (Found: C, 55.36; H, 4.95; N, 3.62. $C_{17}H_{19}MoNO_2$ requires C, 55.89; H, 5.21; N, 3.84%). IR (Nujol mull, cm^{-1}): 1920 (sh), 1910s, 1815 (sh) and 1805s (ν_{CO}), 1715m (ν_{CN}). ^{1}H NMR (C_6D_6): δ 0.75 (s, 9 H, CMe_3), 2.03 (s, 3 H, Me), 5.24 (pseudo-t, 1 H, J_{app} = 2.9, H_y), 5.59 (br s, 1 H, H_z), 6.23 (br s, 1 H, H_x), 6.35–6.60 (overlapping multiplets, 2 H, H_f and H_g), 6.82 (d, 1 H, ^3J = 8.4, H_h) and 6.89 (d, 1 H, ^3J = 8.4 Hz, H_e). ^{13}C-{^{1}H} NMR (CD_3COCD_3): δ 18.6 (MeC=N), 29.8 (CMe_3), 57.6 (CMe_3), 80.7 (C_z), 81.6 (C_x), 93.9 (C_y), 115.6, 119.0 (C_d and C_i), 123.9, 124.4, 124.9, 125.3 ($C_{e–h}$), 188.5 (MeC=N), 249.5, 252.5 (CO).

$[W(\eta^5\text{-}C_9H_7)\{\eta^2\text{-}C(=NBu^t)Me\}(CO)_2]$ 4 and $[W(\eta^5\text{-}C_9H_7)\{\eta^3\text{-}H_2CC(H)NBu^t\}(CO)_2]$ 6. A mixture of compounds **4** and **6** in benzene was generated during the thermolysis of **2** (1.0 g, 2.2 mmol) at 80 °C for 3 h by a procedure analogous to that described above for the conversion of **1** into **3** (and **5**). However, in contrast to the above, all attempts at the fractional crystallization of the products from their admixture proved unsuccessful, separation of the constituents being achieved by means of low-temperature column chromatography. The red-brown mixture of **4** and **6** dissolved in diethyl ether (*ca.* 10 cm^3) was transferred to a column of alumina (20 × 2 cm diameter) that had been precooled to −30 °C. Elution with light petroleum–diethyl ether (5 : 1) separated **4** and **6** as red and yellow bands respectively; **6** eluted first as an intense yellow-brown solution, **4** being recovered from the column as a dark red solution when the concentration of diethyl ether in the eluent was increased. Both fractions were evaporated to dryness and the products redissolved in light petroleum, concentrated as before and cooled to −30 °C overnight giving pure **4** and **6** as red and dark brown crystals respectively.

Compound **4**: yield 0.41 g (41%) (Found: C, 45.00; H, 4.19;

Table 3 Crystal and refinement data * for complexes **2** and **4**

	2	**4**
Formula	$C_{17}H_{19}NO_2W$	$C_{17}H_{19}NO_2W$
M	453.2	453.2
Space group	$P2_1/c$	$P2_1/n$
a/Å	12.926(4)	20.86(3)
b/Å	6.940(4)	9.003(1)
c/Å	19.47(1)	8.617(1)
β/°	101.35(3)	95.96(1)
U/Å^3	1712(1)	1610(2)
D_c/g cm^{-3}	1.76	1.87
μ(Mo-Kα)/cm^{-1}	68.9	73.3
Crystal size/mm	0.2 × 0.2 × 0.2	0.3 × 0.2 × 0.2
Data collected	(−26, 0, 0) to (26, 11, 23)	(−26, 0, 0) to (26, 11, 11)
Unique data	3836	3.29
Observed reflections	1931	2840
R_{int}	0.034	0.045
Standard reflections	3 every 47	3 every 51
$R = \Sigma\|\Delta^2F\|/\Sigma\|F_o\|$	0.045	0.024
$R' = (\Sigma w/\Delta^2F/\Sigma w\|F_o\|^2)^{\frac{1}{2}}$	0.053	0.032
Maximum shift/error	0.002	0.004
Absorption correction range	0.74–1.20	0.85–1.26

* Details in common: M = 453.2; monoclinic; Z = 4; $F(000)$ = 872; 295 K; graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); ω–2θ scans; 2θ range 1–54°; unit weights.

N, 3.08. $C_{17}H_{19}NO_2W$ requires C, 45.03; H, 4.19; N, 3.09%). IR (Nujol mull, cm^{-1}): 1904s, 1896s, 1798s and 1790s (ν_{CO}), 1684w (ν_{CN}). ^{1}H NMR: (C_6D_6, 20 °C); δ 0.74 (s, 9 H, CMe_3), 1.99 (s, 3 H, Me), 5.16 (pseudo-t, 1 H, J_{app} = 2.8, H_y), 5.78 (br m, 1 H, H_z), 6.37 (overlapping multiplets, 2 H, H_x and H_f), 6.55 (m, 1 H, H_g), 6.68 (m, 1 H, H_h) and 6.82 (m, 1 H, H_e); (CD_3COCD_3, −60 °C), δ 0.98 (s, 9 H, CMe_3), 2.41 (s, 3 H, Me), 5.43 (pseudo-t, 1 H, J_{app} = 2.8, H_y), 6.36 (br m, 1 H, H_z), 6.87 (pseudo-t, 1 H, J_{app} = 7.7, H_f), 7.03 (br m, 1 H, H_x), 7.11 (pseudo-t, 1 H, J_{app} = 7.6, H_g), 7.31 (d, 1 H, ^3J = 8.5, H_h) and 7.44 (d, 1 H, ^3J = 8.5 Hz, H_e). ^{13}C-{^{1}H} NMR (C_6D_6): δ 16.7 (Me), 29.2 (CMe_3), 54.9 (CMe_3), 76.0 (C_z), 77.5 (C_x), 91.3 (C_y), 113.8, 119.2 (C_d and C_i), 122.9, 123.0 (C_f and C_h), 124.3 (C_e), 125.2 (C_g), 188.4 (Me*C*=N), 240.7, 243.2 (CO).

Compound **6**: yield 0.16 g (16%) (Found: C, 45.40; H, 4.33; N, 3.03. $C_{17}H_{19}NO_2W$ requires C, 45.03; H, 4.19; N, 3.09%). IR (Nujol mull, cm^{-1}): 1950s and 1867s (ν_{CO}). ^{1}H NMR (CD_3COCD_3): δ 0.17 [dd, 1 H, H_a, $^3J(H_aH_s)$ = 1.6, $^3J(H_aH_c)$ = 6.8 Hz], 1.18 (s, 9 H, CMe_3), 3.32 [dd, 1 H, H_s, $^3J(H_sH_c)$ = 4.3], 5.07 (dd, 1 H, H_c), 5.83 (pseudo-t, 1 H, H_y, J_{app} = 2.8 Hz), 5.97 (br m, 1 H, H_z), 6.56 (br m, 1 H, H_x) and 7.10–7.40 (overlapping multiplets, 4 H, $H_{e–h}$). ^{13}C-{^{1}H} NMR (CD_3COCD_3): δ 31.6 (CMe_3), 39.5 (CH_2, $^1J_{CH}$ = 158), 58.0 (CMe_3), 73.7 (C_z), 76.5 (C_x), 89.4 (C_y), 117.0 (CH_c, $^1J_{CH}$ = 166 Hz), 118.8, 121.9 (C_d and C_i), 125.6, 126.5, 127.0, 127.6 ($C_{e–h}$), 237.3, 237.4 (CO).

Crystallography

Crystallographic data for complexes **2** and **4** are summarized in Table 3. Suitable single crystals were coated with an epoxy resin and mounted in a Enraf-Nonius Kappa diffractometer. The cell dimensions were refined by least-squares fitting the 2θ values of 25 reflections with ranges 10–30 (**2**) and 10–40° (**4**). The intensities were corrected for Lorentz–polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for ω were taken from ref. 24. In each case the position of the heavy atom was obtained from a detailed study of the Patterson function. The rest of the structures were solved by means of Fourier synthesis. An empirical absorption correction[25] was applied at the end of the isotropic refinements. A final refinement was undertaken with unit weights and anisotropic thermal motion for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions determined by molecular geometry. No trend in ΔF *vs.* F_o or sin θ/λ was observed. The final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-RAY 80 system.[26]

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