

Organonitrogen Groups in Metal Carbonyl Complexes. Part IV. Isomeric Forms of Aza-Allyl-Allene † Complexes of Molybdenum and Tungsten

By H. R. Keable and M. Kilner,* Department of Chemistry, University of Durham, South Road, Durham City

Reactions between $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}$ or W) and $(p\text{-tolyl})_2\text{C:NLi}$ produce three types of complexes, $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{NC}(p\text{-tolyl})_2]$ (I), $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ (II), and $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}(p\text{-tolyl})_2\text{CO}]$ (III). Two forms of (II; $\text{M} = \text{W}$) were isolated in the solid state but a common species was formed in solution. (III) also gave the same solution species together with the free ketone. A mechanism for the formation of the complexes and the biproducts $(p\text{-tolyl})_2\text{CO}$, NCO^- , and CN^- is proposed. All complexes failed to undergo substitution reactions with Ph_3P .

FOLLOWING the synthesis of the first aza-allyl-allene derivative $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{Ph}_2\text{CNCPh}_2)]$ ¹ attempts were made to study the nature of the bonding of the nitrogen ligand to the metal by replacing phenyl groups by *t*-butyl groups in order to use the latter as ¹H n.m.r. probes.² Reactions of $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}$ or W) with $\text{Bu}^t\text{PhC:NLi}$ or $\text{Bu}^t_2\text{C:NLi}$ produced only the mononuclear methyleneamino-complexes $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{N:C}(\text{Bu}^t)\text{R}]$ ($\text{R} = \text{Ph}$ or Bu^t).^{2,3} Steric factors may be responsible for the different course of the reactions, but based upon a limited range of methyleneamines studied, the presence of aryl substituents appears an important factor in the formation of aza-allyl-allene complexes by this route. Consequently we chose to study the di-*p*-tolylmethyleneamine derivatives to use the *p*-Me groups as probes for a ¹H n.m.r. study. We

† Throughout this paper the nomenclature of the organonitrogen group $[\text{R}_2\text{CNCR}_2]$ 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, $\text{R}_2\text{CC}(\text{H})\text{CR}_2$], and the term *aza-allene* to the group when the R_2C planes are perpendicular. The latter group is formally derived from $[\text{R}_2\text{C}=\overset{\ddagger}{\text{N}}=\text{CR}_2]$, the dialkylideneammonium ion, which is isoelectronic and isostructural with allenes, $\text{R}_2\text{C}=\text{C}=\text{CR}_2$.

now report the synthesis of two forms of the aza-allyl-allene complexes and the new type of complex $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}(p\text{-tolyl})_2\text{CO}]$ ($\text{M} = \text{Mo}$ or W). Valuable information concerning the bonding of the aza-allyl-allene ligand in the complexes in solution was obtained by n.m.r. spectroscopy and will be reported in detail in a later paper.

The products isolated from the reaction of $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}$ or W) with $[(p\text{-tolyl})_2\text{C:NLi}]$ show a marked contrast to those obtained from the corresponding reaction with $\text{Ph}_2\text{C:NLi}$,¹ and indicate that the introduction of a *p*-Me substituent into the aromatic ring has a distinct effect on the course of the reaction.

RESULTS AND DISCUSSION

Reaction of $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}$ or W) with $[\text{Ph}_2\text{C:NLi}]$ produced only the aza-allyl-allene derivatives

¹ K. Farmery, M. Kilner, and C. Midcalf, *J. Chem. Soc. (A)*, 1970, 2279; K. Farmery and M. Kilner, *J. Organometallic Chem.*, 1969, 16, p. 51.

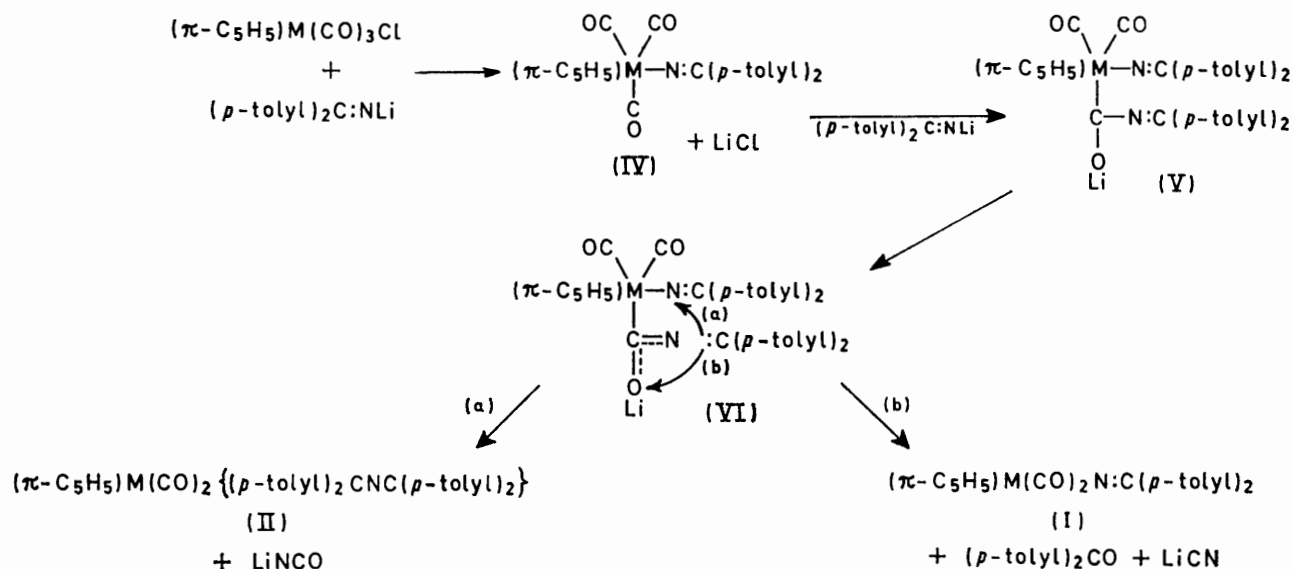
² M. Kilner and C. Midcalf, *Chem. Comm.*, 1970, 552; *J. Chem. Soc. (A)*, 1971, 292.

³ M. Kilner and J. N. Pinkney, *J. Chem. Soc. (A)*, 1971, 2887.

$[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{Ph}_2\text{CNCPh}_2)]$, no other carbonyl products being detected, whilst the reaction with $[\text{Ph}_2\text{C}:\text{NSiMe}_3]$ produced $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})\text{N}:\text{CPh}_2]_2$ and $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{N}:\text{CPh}_2]$.¹ In contrast, the reaction with $[(p\text{-tolyl})_2\text{C}:\text{NLi}]$ gave three carbonyl products $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{N}:\text{C}(p\text{-tolyl})_2]$ (I), $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ (II) and $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}(p\text{-tolyl})_2\text{CO}]$ (III), no reaction being observed with $[(p\text{-tolyl})_2\text{C}:\text{NSiMe}_3]$. The three products have sufficiently different solubilities to allow fractional crystallisation, from hexane-monoglyme or ether mixtures, to be employed as a method of separation. Complex (III) is the final material to be obtained from the mother liquor, not unexpectedly since in solution dissociation to (II) and free ketone occurs. Consequently complex (III) will only crystallise when the ketone is in large excess, *i.e.* when the bulk of (II) has already been removed from solution, and the volume of solution has been reduced drastically.

$\nu(\text{CO})$ frequencies are lower than for the diphenyl compound,¹ indicating that replacement of the ring hydrogens by *para*-methyl groups produces the expected increase in electron density on the metal. The upfield shift of the $\pi\text{-C}_5\text{H}_5$ resonance in the ^1H n.m.r. spectrum (τ 4.0 \rightarrow 4.09, for the tungsten complexes) is also indicative of a flow of electron density to the metal,⁴ and is consistent with the correlation between the Hammett σ constants of the substituents X and the $\pi\text{-C}_5\text{H}_5$ shift observed recently for compounds of the type $\text{X-C}_6\text{H}_4\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$.⁵ Only a single methyl resonance appears in the n.m.r. spectrum of (I), no indication of line broadening being observed in the range from -40 to $+40^\circ$. A linear M-N-C skeleton is indicated, as has been shown by X-ray diffraction for $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{N}:\text{CBu}^t_2]$.⁶

No reaction was observed between (I) and I_2 or Ph_3P , non-carbonyl decomposition products being obtained. The complex thus behaves very similarly to the



SCHEME

Complexes (I) and (II) were prepared by adding a solution of $(p\text{-tolyl})_2\text{C}:\text{NLi}$ to a solution of $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}$ or W). The ratio of the yield of (I) to that of (II) depends on the temperature of mixing and on whether M is Mo or W . Most studies on complex (I) were undertaken using the molybdenum complex as this was the easier to obtain pure in large quantities, though sufficient of the tungsten complex was obtained to allow complete characterisation.

$[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{N}:\text{C}(p\text{-tolyl})_2]$ (I).—The complexes were obtained as dark blue crystals, stable for long periods in air, although solutions decomposed rapidly to brown non-carbonyl materials on exposure to air. I.r. and ^1H n.m.r. data are given in the Table. The

⁴ R. B. King, *New Aspects Chem. Metal Carbonyl Deriv.*, Intern. Symp. Proc., 1968, E6.

⁵ Elisabeth S. Bolton, G. R. Knox, and C. G. Robertson, *Chem. Comm.*, 1969, 664.

diphenyl derivatives¹ and contrasts with the Bu^t derivatives for which $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})\text{I}_2(\text{N}:\text{CBu}^t\text{R})]$ ($\text{M} = \text{Mo}$ or W ; $\text{R} = \text{Bu}^t$ or Ph)^{2,3} and $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PPh}_3)(\text{N}:\text{CBu}^t\text{Ph})]$ ³ were formed. On heating a monoglyme solution of (I), no dinuclear species of the type $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})\text{N}:\text{CR}_2]_2$ could be obtained, as occurs for the diphenyl system.¹ The bulk of the material was recovered unchanged along with some non-carbonyl decomposition products.

$[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ (II).—Dropwise addition of an ether solution of $[(p\text{-tolyl})_2\text{C}:\text{NLi}]$ to an ether solution of $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Cl}]$ ($\text{M} = \text{Mo}$ or W) at room temperature produces (II) almost exclusively. Crystallisation from ether-hexane mixtures affords small deep purple, air-stable crystals. A small quantity

⁶ H. M. M. Shearer and J. D. Sowerby, personal communication.

of complex (III) is usually obtained as a final crop of crystals. Complex (II) is moderately soluble in hexane and other aliphatic hydrocarbons, and very soluble in most other organic solvents giving very intense purple solutions. ¹H N.m.r. spectra for the tungsten complex at

shown in Figure 1. Solution spectra in solvents other than hexane show that both isomers form a common species in solution and that this species bears a far greater resemblance to the solid-state form B. No evidence has been found for this form for M = Mo.

Spectroscopic data

Complex	I.r.		¹ H n.m.r. ^a		
	Form	$\nu(\text{CO})/\text{cm}^{-1}$	$\tau(\text{Ph})^b$	$\tau(\text{C}_5\text{H}_5)$	$\tau(\text{Me})$
[(π -C ₅ H ₅)Mo(CO) ₂ NC(<i>p</i> -tolyl) ₂]	KBr	1949s, 1855s	2.70(8) ^c	4.13(5) ^c	7.57(6) ^c
	CS ₂ soln.	1965s, 1883s			
[(π -C ₅ H ₅)W(CO) ₂ NC(<i>p</i> -tolyl) ₂]	KBr	1938s, 1838s	2.82(8) ^c	4.09(5) ^c	7.59(6) ^c
	CS ₂ soln.	1948s, 1866s			
[(π -C ₅ H ₅)Mo(CO) ₂ {(<i>p</i> -tolyl) ₂ CNC(<i>p</i> -tolyl) ₂ }]	KBr	1936s, 1821s	2.92(16)	5.54(5)	7.49(3), 7.73(3), 7.82(3), 7.86(3)
	CS ₂ soln.	1938s, 1844s			
[(π -C ₅ H ₅)W(CO) ₂ {(<i>p</i> -tolyl) ₂ CNC(<i>p</i> -tolyl) ₂ }] Form A	Hexane soln.	1949s, 1856s, br	2.92(16)	5.45(5)	7.48(3), 7.71(3), 7.81(3), 7.85(3)
	KBr	1934s, 1815s			
[(π -C ₅ H ₅)W(CO) ₂ {(<i>p</i> -tolyl) ₂ CNC(<i>p</i> -tolyl) ₂ }] Form B	CS ₂ soln.	1932s, 1838s	2.92(16)	5.45(5)	7.48(3), 7.71(3), 7.81(3), 7.85(3)
	Hexane soln.	1944s, 1850s, br			
[(π -C ₅ H ₅)Mo(CO) ₂ {(<i>p</i> -tolyl) ₂ CNC(<i>p</i> -tolyl) ₂ }(<i>p</i> -tolyl) ₂ CO]	KBr	1919s, 1832s	2.82(24) ^d	5.50(5)	7.49(3), 7.73(3), 7.82(3), 7.86(3), 7.58(6)
	CS ₂ soln.	1938s, 1844s			
[(π -C ₅ H ₅)W(CO) ₂ {(<i>p</i> -tolyl) ₂ CNC(<i>p</i> -tolyl) ₂ }(<i>p</i> -tolyl) ₂ CO]	Hexane soln.	1949s, 1856s, br	2.82(24) ^d	5.41(5)	7.48(3), 7.71(3), 7.81(3), 7.85(3), 7.58(6)
	KBr	1917s, 1830s			
	CS ₂ soln.	1932s, 1838s			
	Hexane soln.	1944s, 1850s, br			

^a CS₂ Solution at -20°. ^b Multiplet. ^c CDCl₃ Solution at 36°. ^d Average value of multiplet due to aza-allyl and ketone groups.

a range of temperatures are shown in Figure 1 of reference 7—a more detailed discussion of these results will be presented in due course.

Two forms exist in the solid state (forms A and B). The product of the reaction for M = Mo is form A, and for M = W, form B results, providing a co-ordinating

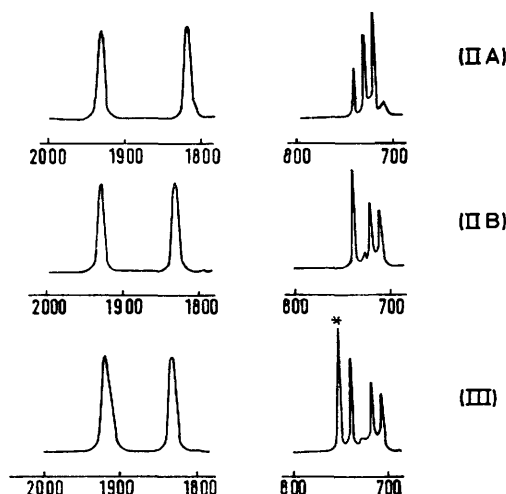


FIGURE 1 I.r. data for tungsten complexes (KBr discs)

* Present also for the free ketone

solvent (*e.g.* ether or monoglyme) is used in the crystallisation process. If hexane only is used form A results. Solid-state i.r. spectra (KBr disc) are sufficiently different to indicate the occurrence of isomers rather than crystalline modifications. The major differences are

The apparent difference between the molybdenum and tungsten systems is unlikely to be due to steric factors as the effective sizes of molybdenum and tungsten are very similar, due to the lanthanide contraction. The precise nature of forms A and B need to be determined before the question of the factors influencing their formation can be answered, and to this end the crystal structure of form A (M = Mo) has been completed and that of form B (M = W) is in progress.⁶

Form A has an aza-allene group rather than an aza-allyl group (see Figure 2)—the planes of the -CR₂ groups are perpendicular. The two carbon-nitrogen bond lengths correspond essentially to a single and a double bond with $\widehat{\text{CNC}} = 128^\circ$. The Mo-C and Mo-N bond lengths are slightly less than accepted single-bond lengths⁶ indicating extensive back donation into ligand anti-bonding orbitals (*cf.* tetracyanoethylene complexes).⁸

The distinction between π -aza-allyl and π -aza-allene ligands would appear to be much less pronounced than that between the π -allyl and π -allene ligands. The π -allyl ligand is necessarily bent due to sp^2 hybridisation at the central skeletal carbon atom, and is a three-electron donor.⁹ However the π -allene ligand occurs in complexes as a mono-olefin type ligand (*i.e.* a two-electron donor). The adjacent carbon atom not involved in bonding to the metal is displaced away from the metal due to electron donation from the metal to the anti-bonding orbitals of the ligand, and the C:C non-bonding group still retains essentially double-bond character.¹⁰

⁹ M. L. H. Green and P. L. I. Nagy, *Adv. Organometallic Chem.*, 1965, **2**, 325.

¹⁰ T. G. Hewitt and J. J. De Boer, *J. Chem. Soc. (A)*, 1971, 817; J. A. Osborne, *Chem. Comm.*, 1968, 1231.

⁷ H. R. Keable and M. Kilner, *Chem. Comm.*, 1971, 349.

⁸ W. H. Baddley, *Inorg. Chim. Acta Rev.*, 1968, **2**, 7.

The π -aza-allyl ligand can act as a three-electron donor, either through a 3-atom delocalised π -system or σ - π type of interaction. All R groups will be in the same plane and the CNC skeleton linear or bent depending on the extent of involvement of the lone pair of electrons on nitrogen. Alternatively an electron can be considered to be transferred to the metal from the organonitrogen group which, as the aza-allene group $[\text{R}_2\text{C}^+\text{N}:\text{CR}_2]$, then acts as a two-electron donor, or the ligand in this bonding mode may be regarded as a three-electron donor with a C-metal σ -bond and N-metal donor bond. The planes of the two CR_2 groups will be perpendicular for this type of bonding mode and by analogy with observations made on π -allene complexes one might expect the 'free' CR_2 unit to be displaced away from the metal. Interconversion of an aza-allyl form with that of an aza-allene form can be envisaged through a rotation process (90°) of one CR_2 group and the appropriate redistribution of electrons. Indeed, the rotation mechanism proposed to account for the n.m.r. observations⁷ passes through both structures. The low-temperature form would appear to be the aza-allyl species as four methyl peaks would be unlikely to arise for an aza-allene structure.

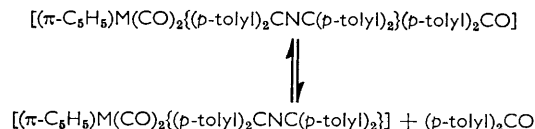
$[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}(p\text{-tolyl})_2\text{CO}]$ (M = Mo or W) (III).—The ketone complexes were isolated for both molybdenum and tungsten, as purple, air-stable crystals. The melting points are sharp indicating an actual complex rather than just a mixture of complex (II) and free ketone. This view is further supported by solid-state i.r. (see Figure 1) and ^1H n.m.r. evidence. The $\nu(\text{CO})$ stretching frequencies are significantly different from those of the corresponding $[(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ complexes and also $\nu(\text{CO})$ at 1645 cm^{-1} for the ketone is slightly lowered from the free-ketone value [$\Delta\nu(\text{CO})$ ca. 15 cm^{-1}] indicating weak co-ordination to the metal.¹¹ The spectrum in the $700\text{--}750\text{ cm}^{-1}$ region, when the ketone absorptions (measured for the free ketone) are subtracted, is identical to that observed for complex (II) (form B). As form B for M = Mo could not be isolated, (III) is unlikely to be a mixture. In the ^1H n.m.r. spectrum, integration of methyl signals arising from the ketone suggests a precise 1 : 1 complex, which is confirmed by analytical data.

On heating solid (III) *in vacuo* to 110° , white crystals were deposited on the cooler parts of the apparatus and were identified by i.r. and mass spectroscopy and elemental analyses as di-*p*-tolylketone. The residues for both the molybdenum and tungsten complexes were shown by i.r. spectroscopy to be the corresponding complexes (II) (form A). Heating form B in the solid state did not produce form A. It would seem that the disruption of the lattice necessary to release the ketone from (III) allows the complex to reform preferentially as form A, presumably the thermodynamically more stable form.

¹¹ W. Hieber and F. Stanner, *Chem. Ber.* 1970, **103**, 2836.

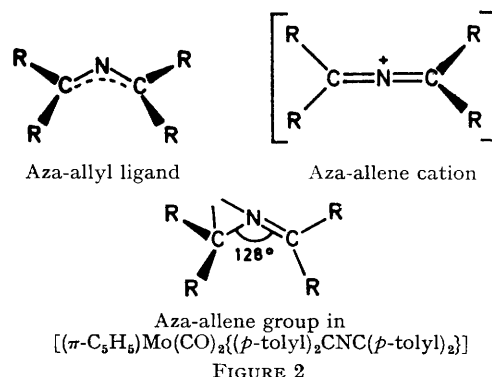
¹² S. Fukuoka, M. Ryang, S. Tsutsumi, *J. Org. Chem.*, 1968, **33**, 2973; E. O. Fischer and H. J. Kollmeier, *Angew. Chem. Internat. Edn.*, 1970, **9**, 309.

In solution (III) dissociates according to:



The presence of an equilibrium is indicated by the following factors. (i) The mixing of equimolar solutions of (II) and the ketone followed by a process of crystallisation results in the recovery of (II) with no (III) whereas if a large excess of ketone is used, (III) alone can be crystallised from the solution. (ii) I.r. solution spectra of (III) are identical to (II) when peaks due to free ketone are subtracted. $\nu(\text{C}=\text{O})$ corresponds to the free ketone value. (iii) The ^1H n.m.r. spectrum in CS_2 solution shows the same variable-temperature behaviour as (II) for the aza-allyl methyl groups⁷ and the position of the methyl resonance arising from the ketone corresponds exactly to the free ketone position, measured under similar conditions.

The ketone is formed during the reaction, its presence as a hydrolysis product in the methyleneamine used having been eliminated by use of a methyleneamino-lithium solution prepared from *p*-tolyl-lithium and *p*-toluonitrile, which still resulted in formation of compound (III). Atmospheric hydrolysis is unlikely as reactions were performed with rigorous exclusion of oxygen



and moisture. The mechanism of the formation of the aza-allyl-allene ligand itself is not yet clear. It is almost certain to take place at the metal, as one of the carbonyl groups is lost as NCO^- and also possibly as CN^- . If initial co-ordination of one methyleneamine unit occurs with elimination of Cl^- (see Scheme) then attack of a further methyleneamine unit at a carbonyl carbon atom may be envisaged (IV). Similar attack of LiNR_2 molecules at metal carbonyl groups is well established and is a route to carbamoyl complexes.¹² Breakdown of the $\text{C}=\text{N}$ system of (V) resulting in formation of a carbene intermediate may then occur followed by attack of this carbene moiety (VI) at the nitrogen of the other co-ordinated methyleneamine unit, forming (II) and eliminating the cyanate ion. Alternatively the carbene may attack the oxygen of the carbonyl group, resulting in formation of the ketone, complex (I), and the cyanide

ion—all observed products. Studies are continuing to resolve this problem.

Reaction to form carbonyl derivatives could not be effected between complexes (II) or (III) and PPh_3 in polar or non-polar solvents even over prolonged periods under forcing conditions. Starting materials were recovered in high yields. These attempted reactions illustrate the stability of the aza-allyl-allene systems towards carbonyl substitution, oxidation, and thermal decomposition.

EXPERIMENTAL

Di-*p*-tolylmethyleneamine,¹³ the lithio-¹⁴ and trimethylsilyl-¹⁵ derivatives were prepared according to published methods and π -cyclopentadienyltricarbonyl-molybdenum and -tungsten chlorides by methods already recorded.¹⁶ Triphenylphosphine was recrystallised from hexane before use. Hydrocarbon solvents and diethyl ether were dried over extruded sodium and monoglyme freshly distilled from lithium aluminium hydride. 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 on a Perkin-Elmer 457 spectrophotometer and ^1H n.m.r. spectra at 60 MHz with a Perkin-Elmer R10 or Varian A56/60D spectrometer. Mass spectra were 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°.

Analyses.—Carbon, hydrogen, and nitrogen were determined with a Perkin-Elmer 240 Elemental Analyser; nitrogen was also determined by the Kjeldahl method. Molecular weights were determined osmotically using a Mechrolab Osmometer, in chloroform or benzene solution.

Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3\text{Cl}]$ with $[(p\text{-tolyl})_2\text{C:NLi}]$, Starting at Low Temperature.—A solution of $[(p\text{-tolyl})_2\text{C:NLi}]$ was prepared by the addition of *n*-butyl-lithium (4.3 mmoles) in hexane (1.9 ml.) to $[(p\text{-tolyl})_2\text{C:NH}]$ (0.90 g., 4.3 mmoles) in diethyl ether (40 ml.) at -78° , the mixture being stirred at room temperature for 15 min. The solution was added to a frozen solution (-196°) of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3\text{Cl}]$ (1.21 g., 4.3 mmoles) in ether (70 ml.) which was then allowed to warm up slowly to room temperature. The solution turned a greenish brown with deposition of a white solid and slow evolution of gas. The reaction was shown to be complete by i.r. spectroscopy after 20 hr. at room temperature. The filtered reaction mixture was evaporated to dryness and the oily residue was extracted with hexane (5 × 10 ml.). Filtration gave a green solution and a red powder, which was shown to be the dimer $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3]_2$ (0.11 g., 10%). On cooling the solution to 0°, deep blue crystals of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2\text{N:C}(p\text{-tolyl})_2]$ separated and were recrystallised from hexane-monoglyme (0.64 g., 35%), m.p. 113° (decomp.) [Found: C, 62.15; H, 4.3; N, 3.6%; *M* (osmotically in chloroform), 421. $\text{C}_{22}\text{H}_{19}\text{MoNO}_2$ requires C, 62.2; H, 4.45; N, 3.3%; *M*, 425], *m/e* (P^+): ^{98}Mo , 427. The corresponding reaction using $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_3\text{Cl}]$ gave two complexes on fractional

crystallisation: (a) $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_2\text{N:C}(p\text{-tolyl})_2]$ (0.12 g., 12%), m.p. 180–182° (decomp.) [Found: C, 51.8; H, 3.65; N, 2.85%; *M* (osmotically in benzene), 519. $\text{C}_{22}\text{H}_{19}\text{WNO}_2$ requires C, 51.45; H, 3.75; N, 2.75%; *M*, 513], *m/e* (P^+): ^{184}W , 513; (b) $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_2\{(p\text{-tolyl})_2\text{C:N:C}(p\text{-tolyl})_2\}]$ (0.41 g., 31%) described below.

Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3\text{Cl}]$ with $[(p\text{-tolyl})_2\text{C:NLi}]$ Starting at Room Temperature.—A solution of $[(p\text{-tolyl})_2\text{C:NLi}]$ (4.3 mmoles) in ether (40 ml.) was prepared as above and was added dropwise to a stirred solution of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_3\text{Cl}]$ (0.61 g., 2.15 mmoles) at room temperature. The solution became purple within minutes and i.r. spectroscopy showed that a different product to the one described above was being formed, the reaction being complete in 2 hr. The reaction mixture was filtered leaving a grey-white residue which contained NCO^- , Cl^- , and also CN^- . The filtrate was evaporated to an oil, extracted with a hexane-monoglyme or ether mixture (6 × 10 ml.) and filtered. Fractional crystallisation at 0° gave firstly, dark purple crystals of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2\{(p\text{-tolyl})_2\text{C:N:C}(p\text{-tolyl})_2\}]$ (0.72 g., 53%), m.p. 190–191° [Found: C, 72.4; H, 5.35; N, 2.2%; *M* (osmotically in benzene), 615. $\text{C}_{37}\text{H}_{33}\text{MoNO}_2$ requires C, 71.75; H, 5.4; N, 2.25%; *M*, 619], *m/e* (P^+): ^{98}Mo , 621; and secondly $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2\{(p\text{-tolyl})_2\text{C:N:C}(p\text{-tolyl})_2\}\text{C=O}]$ (<1%), m.p. 120–121° [Found: C, 75.25; H, 5.7; N, 1.8. $\text{C}_{52}\text{H}_{47}\text{MoNO}_3$ requires C, 75.2; H, 5.65; N, 1.7%].

For the analogous reaction with $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_3\text{Cl}]$ fractional crystallisation gave similar products (a) $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_2\{(p\text{-tolyl})_2\text{C:N:C}(p\text{-tolyl})_2\}]$ (Form B) (0.59 g., 44%), m.p. 128–132° (darkens at 80°) [Found: C, 63.0; H, 4.75; N, 1.9%; *M* (osmotically in benzene), 726. $\text{C}_{37}\text{H}_{33}\text{WNO}_2$ requires C, 62.8; H, 4.7; N, 2.0%; *M*, 707], *m/e* (P^+): ^{184}W , 707.

(b) $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_2\{(p\text{-tolyl})_2\text{C:N:C}(p\text{-tolyl})_2\}\text{C=O}]$ (<1%), m.p. 139–140° [Found: C, 68.05; H, 5.05; N, 1.65. $\text{C}_{52}\text{H}_{47}\text{WNO}_3$ requires C, 68.0; H, 5.1; N, 1.55%].

Action of Heat on $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2\text{N:C}(p\text{-tolyl})_2]$ in Monoglyme Solution.—No reaction was observed in refluxing monoglyme over 28 hr. Starting material was recovered along with some decomposition.

Attempted Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2\text{N:C}(p\text{-tolyl})_2]$ with Triphenylphosphine (1:1 Molar Ratio).—The complex (0.09 g.) was dissolved in hexane (45 ml.) and triphenylphosphine (0.0555 g.) in hexane (15 ml.) was added. No reaction occurred on stirring at room temperature. Refluxing led only to decomposition products.

Attempted Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CO})_2\text{N:C}(p\text{-tolyl})_2]$ with Iodine.—The complex (0.425 g., 1 mmole) was dissolved in monoglyme (30 ml.) and a solution of iodine (0.25 g., 2 mmole) in monoglyme (15 ml.) was added to it. Gas evolution occurred at room temperature and a yellow-white solid was deposited which was shown to be decomposition material.

Attempted Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_3\text{Cl}]$ (*M* = Mo or W) with $[(p\text{-tolyl})_2\text{C:NSiMe}_3]$.—No reaction was observed by i.r. spectroscopy between $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_3\text{Cl}]$ (*M* = Mo, 0.56 g., 2 mmoles; *M* = W, 0.74 g., 2 mmoles) and $[(p\text{-tolyl})_2\text{C:NSiMe}_3]$ (0.56 g., 2 mmoles) in refluxing monoglyme during 72 hr.

Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{C:N:C}(p\text{-tolyl})_2\}]$

¹³ P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, 1961, **26**, 4886.

¹⁴ I. Pattison, K. Wade, and B. K. Wyatt, *J. Chem. Soc. (A)*, 1968, 837.

¹⁵ L-H. Chan and E. G. Rochow, *J. Organometallic Chem.*, 1967, **9**, 231.

¹⁶ T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

(M = Mo [*Form A*], M = W [*Forms A and B*]) with $[(p\text{-tolyl})_2\text{CO}]$.—The complex $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ and a large excess of $[(p\text{-tolyl})_2\text{C:O}]$ (1 : 10 molar ratio) were dissolved in a hexane–monoglyme mixture. Crystallisation at 0° yielded unchanged $[(p\text{-tolyl})_2\text{C=O}]$ and dark purple crystals, m.p. 120–121° (M = Mo); 139–140° (M = W), identified by i.r. spectroscopy as $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}(p\text{-tolyl})_2\text{C=O}]$.

Action of Heat on $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}(p\text{-tolyl})_2\text{C:O}]$ (M = Mo or W).—A small quantity (*ca.* 20 mg.) of complex was placed in a narrow glass tube (5 mm. in diameter) sealed at one end. The tube was evacuated and the solid was heated to *ca.* 110° for 30 min. White crystals formed on the cooler parts of the tube and were

shown to be di-*p*-tolyl ketone by i.r. and mass spectroscopy. The dark purple residue was shown by i.r. spectroscopy to be $[(\pi\text{-C}_5\text{H}_5)_2\text{M}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ [M = Mo, m.p. 190–191°; M = W (form A), m.p. 189–190°].

Attempted Reaction of $[(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CO})_2\{(p\text{-tolyl})_2\text{CNC}(p\text{-tolyl})_2\}]$ with Triphenylphosphine (1 : 1 Molar Ratio).—The complex (0.12 g.) and triphenylphosphine (0.047 g.) were dissolved in a hexane–monoglyme mixture (35 ml.). No reaction was observed during a period of 24 hr. under reflux and starting material were recovered unchanged.

We thank the S.R.C. for a research studentship (to H. R. K.).

[1/1404 Received, August 9th, 1971]