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ORGANOMETALLIC COMPLEXES WITH α-DIIMINES AND RELATED LIGANDS

I. η^3-ALLYLCARBONYL COMPLEXES OF MOLYBDENUM AND TUNGSTEN CONTAINING 1,2-ETHANEDIYLIDENEDIIMINES AS LIGANDS

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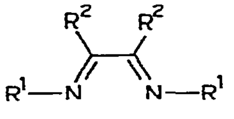
Summary

The complexes $(\eta^3\text{-}C_3H_4R')M(CO)_2(RN{=}CHCH{=}NR)X$ (M = Mo or W; R' = H or Me; R = Me, Et, i-Pr, t-Bu, cyclohexyl, Ph, $p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$; X = Cl, Br, I or NCS) have been prepared and characterized by elemental analysis, solution molecular weight determination and mass spectrometry. Their structures are discussed in the light of their infrared, electronic and ^{1}H NMR spectra. The reactions of the complexes with a number of reagents including MeLi, C_5H_5Tl, $SnCl_2$, Ag^+ and Lewis bases have been investigated.

Introduction

Bidentate ligands of the types I and II, which are closely related to the well known heterocyclic ligands [1—4], 2,2'-bipyridyl (III) and 1,10-phenanthroline (IV), in possessing the common α-diimine moiety, —N=C—C=N—, have hitherto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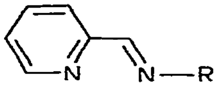
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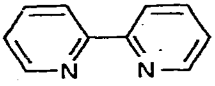
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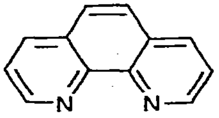
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received relatively little attention [2]. Apart from having similar donor properties and comparable ligand field strenghts [5] to the heterocyclic ligands, the several existing series of coordination complexes [2,5—16] containing ligands of this kind have demonstrated a number of interesting inherent properties such as the intense colour and solvent dependent spectra (solvatochromism) of their metal complexes [6,7,9] and the stabilization of normal and low oxidation states of metals [10—12,15].

Although a number of metal carbonyl complexes with the alipathic α-diimines (I) have been prepared [6—8,10], no organometallic complexes containing these ligands have been reported. Herein we describe the preparation and characterization of the new series of complexes $(\eta^3\text{-}C_3H_4R')M(CO)_2(RN{=}CHCH{=}NR)X$ (M = Mo or W; R′ = H or Me; R = Me, Et, i-Pr, t-Bu, Cyh (= cyclohexyl), Ph, $p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$; X = Cl, Br, I or NCS) and some of their reactions with a variety of reagents; a preliminary account of this work has appeared [17]. The related complexes $(\eta^3\text{-}C_3H_4R)M(CO)_2L_2X$ (M = Cr [18], Mo or W [19—22]; L_2 = bipy or phen) have been previously reported.

Results and discussion

Preparation and some properties of the complexes

Treatment of the acetonitrile complexes $(\eta^3\text{-}C_3H_4R')M(CO)_2(MeCN)_2X$ (M = Mo or W; R′ = H or Me; X = Cl or Br) with the 1,2-ethanediylidenediimines RN=CHCH=NR (R = Me, Et, i-Pr, t-Bu, Cyh, Ph, $p\text{-}MeC_6H_4$ or $p\text{-}MeOC_6H_4$) in warm acetonitrile gives good yields of the complexes $(\eta^3\text{-}C_3H_4R')M(CO)_2\text{-}(RN{=}CHCH{=}NR)X$. An analogous reaction has been previously employed [19] in the synthesis of the 2,2′-bipyridyl and 1,10-phenanthroline complexes which are also accessible by the oxidative elimination reaction [20,21]:

$$fac\text{-}M(CO)_3L_2L' + R'C_3H_4X \rightarrow (\eta^3\text{-}C_3H_4R')M(CO)_2L_2X + CO + L'$$

(L′ = CO or py; L_2 = bipy or phen)

By contrast, the 1,2-ethanediylidenediimine complexes could not be obtained in any significant yield by the latter reaction. The failure of the complexes $(RN{=}CHCH{=}NR)M(CO)_4$ (M = Mo or W) to undergo this and other reactions, e.g. with $HgCl_2$, may be attributed to the larger steric hindrance imposed by the more bulky substituents on the nitrogen atoms.

The iodo and the isothiocyanato derivatives are obtained from the corresponding chloro or bromo complexes by metathesis with sodium chloride and potassium thiocyanate respectively.

Although the chromium complexes $(\eta^3\text{-}C_3H_5)Cr(CO)_2(bipy)X$ (X = Cl, Br, I or NCS) have been recently prepared by the reaction [18]:

$$[(bipy)Cr(CO)_3I]^- + C_3H_5X \rightarrow (\eta^3\text{-}C_3H_5)Cr(CO)_2(bipy)X + CO + I^-$$

Attempts to synthesize the 1,2-ethanediylidenediimine complexes by this or other known procedures have been unsuccessful; in most cases, only the substituted complexes $(RN{=}CHCH{=}NR)Cr(CO)_3L$ (L = MeCN or py) could be isolated.

The new complexes prepared (Table 1) are all very dark blue to almost black

TABLE 1

MELTING POINTS, YIELDS AND ANALYTICAL DATA OF THE COMPLEXES $(\eta^3\text{-}C_3H_4R')M(CO)_2\text{-}(RN{=}CHCH{=}NR)X$

Complex				M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)				Mol. wt [a] found (calcd.)
M	R′	R	X			C	H	N	X	
Mo	H	i-Pr	Cl	191—192	89	42.51 (42.34)	5.65 (5.74)	6.93 (7.60)	9.8 (9.62)	
Mo	H	i-Pr	Br	196—197	92	38.00 (37.78)	5.29 (5.12)	6.86 (6.86)	19.1 (19.34)	415 (413.2)
Mo	H	i-Pr	NCS	>250 [d]	56	43.02 (42.97)	5.34 (5.41)	10.55 (10.74)	8.0 (8.19) [b]	
Mo	Me	i-Pr	Cl	158—159	82	43.52 (43.92)	6.06 (6.06)	6.93 (7.32)	9.1 (9.26)	
Mo	Me	i-Pr	Br	160—161	73	39.45 (39.36)	5.26 (5.43)	6.54 (6.56)	18.6 (18.71)	
Mo	Me	i-Pr	I	163—164	96	35.55 (35.46)	4.87 (4.89)	6.04 (5.91)	26.4 (26.76)	470 [c] (474.2)
Mo	H	t-Bu	Cl	174—175	76	45.68 (45.39)	6.19 (6.35)	6.93 (7.07)	9.2 (8.93)	399 (396.8)
Mo	H	t-Bu	Br	184—185	83	40.97 (40.83)	5.69 (5.71)	6.25 (6.35)	18.3 (18.11)	443 (441.2)
Mo	H	t-Bu	I	189—190	82	37.29 (36.90)	5.22 (5.16)	5.76 (5.74)	25.6 (25.99)	490 (488.2)
Mo	H	Cyh	Cl	194	90	50.50 (50.83)	6.21 (6.51)	5.99 (6.24)	8.1 (7.90)	451 (448.9)
Mo	H	Cyh	Br	192	91	46.21 (46.26)	5.82 (5.93)	5.53 (5.68)	16.6 (16.20)	
Mo	H	Cyh	I	214—215	92	41.87 (42.24)	5.46 (5.41)	5.46 (5.18)	23.1 (23.49)	542 (540.3)
Mo	H	Cyh	NCS	>250 [d]	89	51.12 (50.95)	6.20 (6.20)	8.52 (8.91)	6.1 (6.80) [b]	465 [c] (471.5)
Mo	Me	Cyh	Cl	160—161	74	51.44 (51.89)	6.71 (6.75)	6.02 (6.05)	7.8 (7.66)	
Mo	Me	Cyh	I	191—192	91	43.11 (43.34)	5.81 (5.64)	5.16 (5.05)	22.8 (22.89)	
Mo	H	p-MeC$_6$H$_4$	Br	>218 dec.	30	49.33 (49.52)	4.28 (4.16)	5.61 (5.50)	15.7 (15.69)	
Mo	H	p-MeOC$_6$H$_4$	Br	>222 dec.	74	46.54 (46.59)	3.86 (3.91)	5.50 (5.18)	15.0 (14.77)	
W	H	i-Pr	Br	189	84	30.69 (31.16)	4.07 (4.22)	5.59 (5.59)	16.1 (15.95)	501 (501.1)
W	H	t-Bu	Cl	165—166	85	37.00 (37.17)	5.14 (5.20)	5.69 (5.78)	6.9 (7.31)	485 (484.7)
W	H	t-Bu	Br	178	93	34.05 (34.04)	4.64 (4.76)	5.40 (5.29)	15.3 (15.10)	529 (529.1)
W	H	Cyh	Br	171—172	64	39.34 (39.26)	5.18 (5.03)	4.82 (4.82)	14.1 (13.75)	581 (581.2)
W	H	p-MeOC$_6$H$_4$	Br	194	55	39.97 (40.08)	3.32 (3.36)	4.39 (4.45)	12.2 (12.70)	629 (629.2)

[a] By mass spectrometry unless otherwise stated: P^+ normalized to ^{98}Mo or ^{184}W. [b] Data for S. [c] By osmometry. [d] Decomposed without melting.

crystalline solids which, with the notable exception of the methyl and the ethyl derivatives, are reasonably air-stable in the solid state. They are sparingly soluble in the more polar solvents imparting an intense blue or green coloration to the air-sensitive solution, and the solubility of the complexes increases in the order Cl < Br < I < NCS. The molecular weights of the more soluble complexes,

TABLE 2

INFRARED SPECTRA OF THE COMPLEXES $(\eta^3\text{-}C_3H_4R')M(CO)_2(RN{=}CHCH{=}NR)X$

Complex				$\nu(CO)$ [a]							Cotton—Kraihanzel force parameters [b]	
M	R'	R	X	KBr disc		CHCl$_3$ solution		MeCN solution			k	k_i
Mo	H	Me	Br	*c*		1949ms	1846mw [d]	*c*			1455	79
Mo	H	Et	Cl	*c*		1944vs	1846s	1947vs	1857s		1451	75
Mo	H	i-Pr	Cl	1919s	1849ms	1941s	1862ms	1944s(sh)	1932s	1853s	1461	70
Mo	H	i-Pr	Br	1915s	1851ms	1943s	1864ms	1938m	1858mw [d]		1464	70
Mo	H	i-Pr	NCS [f]	1932vs	1853s [e]	1947vs	1872s	1944vs	1862s		1473	58
Mo	Me	i-Pr	Cl	1927vs	1850s [e]	1961s	1882ms	1951vs	1869s		1491	61
Mo	Me	i-Pr	Br	1931vs	1856s [e]	1966vs	1890s	1948vs	1867s		1502	59
Mo	Me	i-Pr	I	1944vs	1872s [e]	1965vs	1892s 1	1948vs	1870s		1502	57
Mo	H	t-Bu	Cl	1916vs	1841s	1944ms	1839m [d]	1948vs	1857s		1446	80
Mo	H	t-Bu	Br	1932vs	1856s	1953ms	1868m [d]	1946ms	1858m [d]		1475	66
Mo	H	t-Bu	I	1922vs	1844s [e]	1953s	1875ms	1942vs	1858s		1480	60
Mo	H	Cyh	Cl	1928vs	1845s	1930s	1850ms	1936s	1858m [d]		1443	61
Mo	H	Cyh	Br	1933vs	1851s	1941s	1862ms	1938w	1857vw [d]		1461	61
Mo	H	Cyh	I	1930vs	1857s [e]	1946s	1868ms [d]	*h*			1469	60
Mo	H	Cyh	NCS [g]	1928vs	1865s [e]	1946vs	1872s	1941ms	1861m [d]		1472	57
Mo	Me	Cyh	Cl	1932vs 1843s	1919s(sh)	1959vs	1880s	1946vs	1863s [d]		1488	61
Mo	Me	Cyh	I	1935vs	1858s	1959vs	1885s	1946s	1868m [d]		1492	57
Mo	H	Ph	Cl	*c*		1949ms	1850m [d]	1949vs	1857s		1458	76
Mo	H	*p*-MeC$_6$H$_4$	Br	1940vs	1861s	*h*		*h*				
Mo	H	*p*-MeOC$_6$H$_4$	Br	1941s	1860s	1958m	1884mw [d]	*h*			1491	72
W	H	i-Pr	Br	1907vs	1839s	*h*		*h*				
W	H	t-Bu	Cl	1908vs	1831s	1943vs	1857s	1931vs	1840s		1458	70
W	H	t-Bu	Br	1924vs	1845s	1947s	1862m	1934vs	1845s		1465	65
W	H	Cyh	Br	1922vs	1843s	1937s	1861s	*h*			1457	58
W	H	*p*-MeOC$_6$H$_4$	Br	1930vs	1849s	1957s	1880ms [d]	1941m	1860mw [d]		1487	60

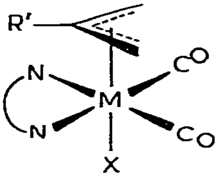
[a] In cm^{-1}. [b] In Nm^{-1} (100 Nm^{-1} = 1 mdyn/Å; calculated using data obtained in CHCl$_3$. [c] Not measured. [d] Saturated solution. [e] In Nujol mull. [f] ν(CN) 2085s (Nujol); 2088s (CHCl$_3$); 2084vs (MeCN) cm^{-1}. [g] ν(CN) 2079s (Nujol); 2091s (CHCl$_3$); 2084m ν(MeCN) cm^{-1}. [h] Insoluble.

(η^3-C_3H_4Me)Mo(CO)$_2$(i-PrN=CHCH=N-i-Pr)I and (η^3-C_3H_5)Mo(CO)$_2$(CyhN=CHCH=NCyh)NCS, in acetone clearly indicate the monomeric nature of these complexes in solution.

Spectra and structure

Most of the complexes are sufficiently volatile at about 200°C to furnish a satisfactory mass spectrum. In addition to the parent ions, species formed by successive loss of carbonyl groups, by loss of the halogen (or pseudohalogen) atom, and by fragmentation of the allyl group as well as the 1,2-ethanediylidene-diimine ligand, are present in the spectra with the bare metal ion, M^+, being generally one of the most intense metal-containing base peaks. Despite the paucity of metastable transitions observed in these spectra, there appears little doubt that these are indeed the major, competitive fragmentation pathways.

The absence of any dimeric species in the mass spectra lends further support to the monomeric nature of these complexes for which four geometrical configurations, V—VIII, are possible.



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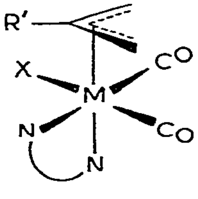

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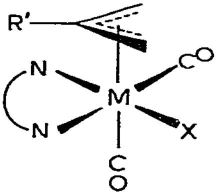

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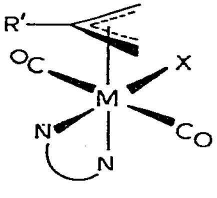

(VIII)

The infrared spectra of the complexes (Table 2) show two almost equally intense carbonyl stretching absorptions both in the solid state and in solution suggesting that the two carbonyl groups are *cis* to each other and that the solid state structure of the complexes is retained in solution. The *trans*-dicarbonyl structure (VIII) may be excluded a priori since a low intensity, higher frequency symmetrical stretch and a very strong, lower frequency asymmetrical stretch are to be expected. In complexes of the type, (R^1N=CR^2CR^2=NR^1)M(CO)$_4$ (M = Mo or W), the two carbonyl groups *cis* to the α-diimine ligands have been shown to be virtually independent of the nature of the solvent [7]. Structures VI and VII may then be ruled out in view of the considerably large solvent dependence found in the infrared spectra of the complexes. The purported configuration V * is also found in the crystal structures of the related complexes, (η^3-C_3H_4Me)-Mo(CO)$_2$(phen)NCS [23] and (η^3-C_3H_5)Mo(CO)$_2$bipyNCS [24], which exhibit ν(CN), ν(CS) and δ(NCS) frequencies similar to those of the complexes, (η^3-C_3H_5)-

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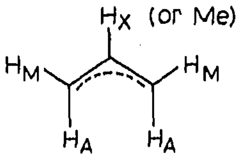
* *Note added in proof:* The crystal structures of several complexes have been determined by Dr. A.J. Graham confirming the configuration V.

TABLE 3

PROTON NMR SPECTRA OF THE COMPLEXES $(\eta^3\text{-}C_3H_4R')M(CO)_2(RN{=}CHCH{=}NR)X$

Complex				Solvent	δ(allyl) [a, b]			δ(α-diimine) [a]		
M	R'	R	X		H_A	H_M	H_X or Me	Me	CH=N	Others
Mo	Me	i-Pr	Cl	$CDCl_3$	1.53s(2)	3.03s(2)	1.67s(3)	1.37d, 1.40d(12) [c]	8.23s(2)	CH, 4.4(2) [d]
Mo	Me	i-Pr	Br	$CDCl_3$	1.56s(2)	3.05s(2)	1.59s(3)	1.35d, 1.43d(12) [c]	8.19s(2)	CH, 4.4(2) [d]
Mo	Me	i-Pr	I	$CDCl_3$	[e]	3.15s(2)	1.53s(3)	1.35d, 1.51d(12) [c]	8.18s(2)	CH, 4.3(2) [d]
Mo	H	t-Bu	Cl	CD_2Cl_2	1.18d(2) [f]	3.45d(2) [g]	[h]	1.50s(18)	8.28s(2)	
Mo	H	t-Bu	Br	CD_2Cl_2	1.21d(2) [f]	3.46d(2) [g]	[h]	1.54s(18)	8.26s(2)	
Mo	H	t-Bu	I	$CDCl_3$	1.32d(2) [f]	3.54d(2) [g]	~3.2m(1)	1.58s(18)	8.23s(2)	
Mo	Me	Cyh	Cl	$CDCl_3$	1.48s(2)	2.97s(2)	1.67s(3)		8.21s(2)	CH_2 ~ vbr(20); CH ~ br(2)
Mo	Me	Cyh	I	$CDCl_3$	1.61s(2)	3.09s(2)	1.51s(3)		8.07s(2)	CH_2 ~ vbr(20); CH ~ br(2)
W	H	t-Bu	Br	$(CD_3)_2CO$	1.37d(2) [f, i]	3.35d(2) [g, i]	[h]	1.58s(18)	8.85s(2)	

[a] In ppm downfield from TMS; relative intensities in parentheses. [b] $R' = H_X$ or Me in



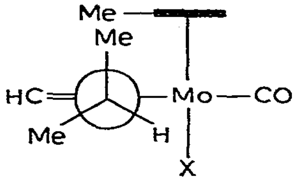
[c] $^3J(HH) = 6.7$ Hz. [d] Apparent septet with $^3J(HH) \sim 7$ Hz. [e] Obscured. [f] $^3J(AX) = 9.0$ Hz. [g] $^3J(MX) = 6.0$ Hz. [h] Not located. [i] $^{183}W\text{—}^1H$ coupling not observed.

$Mo(CO)_2(RN{=}CHCH{=}NR)NCS$ (R = i-Pr or Cyh), indicating that the latter complexes also contain N-bonded isothiocyanate group.

The low solubility of the complexes considerably reduces the viability of an attempt to correlate the solvent effects with shifts in the carbonyl stretching modes through the calculated Cotton—Kraihanzel force parameters (k = stretching force constant; k_i = stretch—stretch interaction constant) [25]. Nevertheless, it given solvent, k and hence the carbonyl bond order, decreases in the following sequences as expected, R = t-Bu > i-Pr > Cyh > Me and X = NCS > I > Br > Cl which, albeit somewhat irregular in some cases, do indicate that the effects of ligands such as X and the substituents on the nitrogen atoms (R) are not altogether undetectable.

The salient features in the electronic spectra of the complexes are the very intense $\pi \rightarrow \pi^*$ ligand charge transfer band [6,12] in the $\lambda_{max} \sim 240$ nm region and the strong absorption ($\lambda_{max} > 550$ nm) assignable to the metal-to-ligand charge transfer [7]. Some shifts are observed for the lower energy absorption with different substituents on the nitrogen atoms. It also appears to undergo a hypsochromic shift with the more polar solvents but no correlation with the polarity of the solvent used could be improvised owing to their low solubilities.

The proton NMR spectra (Table 3) of the most soluble complexes indicate that the allyl group is π-bonded to the Group VI metals. The H_X proton resonance of the allylic A_2M_2X signals is often inconspicuous and detected only through integration. Of particular interest are the spectra of the complexes $(\eta^3\text{-}C_3H_4Me)Mo(CO)_2(i\text{-}PrN{=}CHCH{=}N\text{-}i\text{-}Pr)X$ (X = Cl, Br or I) which exhibit a pair of doublets assignable to the magnetically non-equivalent isopropyl methyl groups as in IX.



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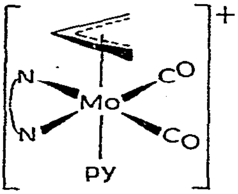
The coordination of the α-diimine ligands to the Group VI metal is substantiated by the downfield shifts (about 0.1—0.2 ppm) in the azomethine proton resonance as previously observed in 1,2-ethanediylidenediimine (L_2) complexes of the types $L_2M(CO)_4$ (M = Mo or W) [26], $XM(CO)_3L_2$ (M = Mn or Re; X = Cl, Br or I) [27] and L_2MX_2 (M = Zn, Cd or Hg; X = Cl, Br or I) [16]. The diamagnetic shifts in all these complexes, together with chemical [28] and ^{13}C NMR evidence [29] described elsewhere, indicate that there is considerable π-delocalization within the five-membered chelate ring formed by the overlapping of the π orbitals of the 1,2-ethanediylidenediimine ligand with the metal d orbitals of appropriate symmetry (d_{xz} and d_{yz}) which in turn interact with the π^* orbitals of the two carbonyl groups. Consequently, any electronic perturbation by solvent or through the substituents on the nitrogen atoms would be reflected in a shift in the carbonyl stretching frequencies, which is indeed observed.

Reactions of the complexes

Sulphur dioxide 'inserts' into the η^3-allyl—metal bonds in complexes such as those of palladium [30], platinum [30,31] and rhodium [31] to afford the corresponding 1-allenesulphinato complexes but forms stable adducts with others such as $(\eta^3\text{-}C_3H_5)Rh(PPh_3)_2Cl_2$ [33]. By contrast, the α-diimine complexes $(\eta^3\text{-}C_3H_4R')Mo(CO)_2$ (RN=CHCH=NR)X (R' = H, R = t-Bu, X = Br; R = Cyh, X = Cl; R' = Me, R = i-Pr, X = Br) slowly dissolve in liquid sulphur dioxide without the formation of either an insertion product or a stable adduct as evident from their NMR spectra.

There is no apparent reaction between the α-diimine complexes and tin(II) or indium(I) halides in tetrahydrofuran at room temperature or when heated under reflux, although these reactions have been well established as a general route to metal—tin or metal—indium bonded complexes [33,34]. Despite the success of the halogen exchange reaction described above, the halide group in the α-diimine complexes does not react with caesium trichlorostannate(II) to give any metal—tin bonded complexes.

However, the halogen atoms in these complexes can be readily abstracted using silver(I) or less effectively, thallium(I) tetrafluoroborate, and in the presence of a suitable donor ligand, L, cationic complexes can be isolated. One of these cationic complexes, $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(CyhN{=}CHCH{=}NCyh)py]BF_4$, has been examined in detail; its elemental analysis, conductivity in acetone solution and infrared spectrum are consistent with its ionic formulation. The stereochemistry of the cation is believed to be X by analogy with that in the related complex, $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(bipy)py]BF_4$, the crystal structure of which has been determined by X-ray analysis [35].



(X)

Treatment of the complexes $(\eta^3\text{-}C_3H_5)Mo(CO)_2(RN{=}CHCH{=}NR)X$ (R = t-Bu, X = Br; R = Cyh, X = Cl) with methyllithium or methylmagnesium iodide gives moisture- and air-sensitive, dark coloured solids * of unknown composition and no metal methyls could be isolated. These complexes also fail to yield any η^1- or η^5-cyclopentadienyl complexes with thallium(I) cyclopentadienide.

No apparent reaction occurs between these α-diimine complexes and triphenylphosphine at room temperature. When treated with more than three-fold excess of triphenylphosphine in acetonitrile, the allyl group is lost and the complexes $(RN{=}CHCH{=}NR)Mo(CO)_2(PPh_3)_2$ (R = i-Pr, t-Bu or Cyh) are formed along with the phosphonium salt $[R'C_3H_4PPh_3]X$. This reaction appears to be much slower than the analogous reaction of $(\eta^3\text{-}C_3H_4R')Mo(CO)_2(MeCN)_2X$ [8].

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* Although the nature of these solids is unknown, they may well be associated with the products (or decomposition products) formed either by the alkylation inter alia of the carbonyl groups or by the reduction of the five-membered chelate ring, a phenomenon recently reported for the complexes $(RN{=}CHCH{=}NR)Mo(CO)_4$ [36].

Unidentate nitrogen-donor ligands such as pyridine or acetonitrile do not react with these complexes. However, the *N*,*N'*-dialkyl-1,2-ethanediylidenediimine ligands of the complexes are displaced by 2,2'-bipyridyl or 1,10-phenanthroline on prolonged heating. Although this may reflect the marginally extra stabilization effect of the heterocyclic ligands through better electron delocalization in the aromatic rings, it must have been further promoted by the very low solubility of the resulting complexes $(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2X$ (L_2 = bipy or phen).

Experimental

All manipulations involving solutions of the complexes were performed under an atmosphere of nitrogen and solvents were dried and deaeriated before use.

The metal hexacarbonyls (Pressure Chemicals), allyl halides (Koch—Light), glyoxal and organic amines (BDH or Koch—Light) were reagentgrade commercial products and used without further purification.

Physical measurements

Infrared spectra (4000—250 cm^{-1}) of the complexes in KBr discs were recorded on a Perkin—Elmer P180 spectrophotometer. Solution spectra in carbonyl stretching region (2100—1800 cm^{-1}) were taken on a Perkin—Elmer 257 spectrophotometer operating on X10 expansion and using a balanced pair of NaCl cells (0.5 mm); calibration was made against CO to give a precision of ±2 cm^{-1}.

Proton NMR spectra were registered on a Varian Associates 56/60A or a HA-100 spectrometer using TMS as an internal standard.

Mass spectra were obtained on a Hitachi—Perkin—Elmer RMU-6E spectrometer operating at a source pressure of 10^{-7} Torr, 70 eV ionizing energy, resolution of 1000 and 8 kV accelerating voltage. Samples were introduced by direct insertion into the heated ion source. The characteristic isotope pattern was observed for each metal-containing ion.

Electronic spectra were scanned on a Unicam SP 800 spectrophotometer in chloroform or acetone in sealed cells. Molecular weights were measured in acetone solution on a Mechrolab 301A Osmometer at 37° C. Conductivity measurements were made using a Wayne—Kerr bridge. Melting points were determined in unsealed capillary tubes using an Electrothermal hot-stage apparatus, and are uncorrected.

Elemental analyses were performed by the Australian Microanalytical Service, Melbourne, and the data are given in Table 1.

Ligand synthesis

The ligands RN=CHCH=NR (R = i-Pr, t-Bu [12, 37, 38], Ph, *p*-MeC_6H_4 [12] and *p*-$MeOC_6H_4$ [7]) were prepared as described in the literature with slight modification.

A 40% aqueous glyoxal solution (0.05 mol) was added to the appropriate amine (0.10 mol) in water (for R = i-Pr, t-Bu or Cyh) or in warm methanol (for R = Ph, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$). The colourless alkyl derivatives were isolated by ether extraction, drying ($MgSO_4$) and removal of the solvent under reduced pressure at 0° C. The lachrymatory isopropyl (m.p. 58—59° C) and t-butyl (m.p.

55° C; lit. [12] 56° C) derivatives were purified by sublimation at ambient temperature/0.1 Torr, while the cyclohexyl compound (m.p. 146—147° C; lit. [12] 146—147° C) was recrystallized from diethyl ether or methanol. Yellow needles of the *p*-tolyl (m.p. 152—153° C dec.) and *p*-anisyl (m.p. 159—160° C; lit. [12] 160—162° C) derivatives were isolated pure from the reaction mixture. The phenyl derivative was obtained as a yellow powder (m.p. 105—106° C dec.; lit. [12] 105—107° C dec.).

Preparation of $(\eta^3\text{-}C_3H_4R')M(CO)_2(MeCN)_2X$

Method A. A solution of $(MeCN)_3M(CO)_3$, obtained by refluxing the appropriate $M(CO)_6$ (0.01 mol) in 50 ml of anhydrous acetonitrile (M = Mo, 18 h; M = W, >48 h), was treated with an equimolar amount of the allyl halide, $R'C_3H_4X$ (R' = H or Me; X = Cl or Br), and the mixture was further heated for 15—20 min [20]. The resulting orange solutions of the complexes were used for further reactions. The complexes may be isolated by partial evaporation of the solvent in vacuo. Yield >90%.

Method B. A mixture of $Mo(CO)_6$ (0.01 mol), $R'C_3H_4X$ (R' = H or Me; X = Cl or Br; 0.01 mol) and 50 ml of anhydrous acetonitrile was heated under reflux for about 4 ± 0.5 h to give an orange solution of $(\eta^3\text{-}C_3H_4R)Mo(CO)_2(MeCN)_2X$ [19]. The course of the reaction was readily monitored by infrared spectroscopy.

Preparation of $(\eta^3\text{-}C_3H_4R')M(CO)_2(RN{=}CHCH{=}NR)X$ *(X = Cl or Br)*

The 1,2-ethanediylidenediimine ligand (0.01 mol) was added as a solution or slurry in 10 ml of anhydrous acetonitrile to a solution of $(\eta^3\text{-}C_3H_4R')M(CO)_2(MeCN)_2X$ (0.01 mol) in the same solvent (50 ml). The resulting dark mixture was warmed (5 min for R = i-Pr or t-Bu) or heated under reflux (10—15 min for R = Cyh, *p*-MeC_6H_4 or *p*-$MeOC_6H_4$). The solution was cooled slowly to room temperature and then to 0° C; the crystalline product was collected by filtration, washed with a 1 : 25 mixture of diethyl ether/light petroleum (b.p. 40—60° C) and dried in vacuo. Yields were generally in the range 55—90%.

Reactions of $(\eta^3\text{-}C_3H_4R')M(CO)_2(RN{=}CHCH{=}NR)X$ *(X = Cl or Br)*

(a) With sodium iodide. In a typical experiment, a mixture of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CyhN{=}CHCH{=}NCyh)Cl$ (0.46 g, 1.02 mmol) and NaI (1.5 g, 10.0 mmol) in 30 ml of acetone was heated under reflux for 45 min. The cooled mixture was evaporated to dryness and the solid residue was broken up and transferred on to a filter. It was successively washed with 100 ml of water and 20 ml of methanol. Recrystallization from hot acetone by slow solvent evaporation gave 0.51 g (92%) of the crystalline iodo complex.

Other iodo complexes were similarly prepared.

(b) With potassium thiocyanate. This reaction was entirely analogous to that described in *a* for the iodo complexes.

(c) With tin(II) halides. A mixture of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(t\text{-}BuN{=}CHCH{=}N\text{-}t\text{-}Bu)Br$ (1.10 g, 2.49 mmol) and $SnBr_2$ (0.69 g, 2.49 mmol) in 50 ml of ethanol was heated under reflux for 0.5 h. The cooled mixture was filtered and evaporated leaving a dark oil which did not solidify. TLC analysis showed the presence of only the starting materials and some decomposition products which did not move on the plate.

(d) With methyllithium. A partial solution of (η^3-C_3H_5)Mo(CO)$_2$(t-BuN=CHCH=N-t-Bu)Br (0.45 g, 1.02 mmol) in 25 ml of dry tetrahydrofuran was treated with a 1.25 *M* solution (1.1 ml, 1.37 mmol) of MeLi. The solution rapidly darkened and all the remaining solid complex dissolved. As the complex is moisture-sensitive, hydrolysis was not attempted. The solvent was removed under reduced pressure to give a pyrophoric dark brown-black solid. Attempted extraction with chloroform, acetone or acetonitrile led to considerable decomposition.

(e) With triphenylphosphine. In a typical reaction, a mixture of (η^3-C_3H_4Me)-Mo(CO)$_2$(i-Pr^{1}N=CHCH=N-i-Pr)Cl (0.45 g, 1.18 mmol) and PPh$_3$ (0.96 g, 3.66 mmol) was heated to reflux in 50 ml of acetonitrile for 2 h during which the solution gradually turned dark red-violet. The mixture was cooled, filtered and the solvent was partially evaporated until crystallization had begun. The product was filtered after cooling to 0° C, and recrystallized from a minimum volume of boiling acetonitrile to afford dark violet crystals of (i-PrN=CHCH=N-i-Pr)Mo-(CO)$_2$(PPh$_3$)$_2$ [8], ν(CO) 1835s, 1754s cm^{-1} (Nujol). (Found: C, 67.24; H, 5.53; N, 3.37: $C_{46}H_{46}MoN_2O_2P_2$ calcd.: C, 67.64; H, 5.68; N, 3.43.)

Other related reactions were similarly performed.

(f) With 2,2'-bipyridyl or 1,10-phenanthroline. An equimolar (1.0 mmol) mixture of (η^3-C_3H_5)Mo(CO)$_2$(t-BuN=CHCH=N-t-Bu)Br and bipy or phen was heated in 50 ml of acetonitrile for 2 h. After cooling, the deposited dark red crystalline solid was filtered, washed with 1 : 25 diethyl ether/light petroleum (b.p. 40—60° C) and dried in vacuo. It was identified spectroscopically to be (η^3-C_3H_5)Mo(CO)$_2$L$_2$Cl (L$_2$ = bipy or phen).

(g) Formation of cationic complexes. In a typical experiment, (η^3-C_3H_5)Mo-(CO)$_2$(CyhN=CHCH=NCyh)Cl (0.87 g, 1.94 mmol) was stirred at room temperature with AgBF$_4$ (0.38 g, 1.94 mmol) in 30 ml of acetone containing a few drops of pyridine. After 0.5 h, the resulting maroon solution was filtered and slowly concentrated under a stream of nitrogen to give black crystals of the cationic complex, [(η^3-C_3H_5)Mo(CO)$_2$(CyhN=CHCH=NCyh)py]BF$_4$ (0.95 g, 84%), Λ_M, 121 ohm^{-1} cm^2 mol^{-1} in 2.5×10^{-4} *M* acetone solution; ν(CO) in acetonitrile: 1959vs 1882 cm^{-1}.

In a similar experiment using TlBF$_4$, a less pure product was obtained (71%).

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