Journal of Organometallic Chemistry, 218 (1981) 337—349
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE REACTION BETWEEN $[\eta^5\text{-}C_5H_5M(CO)_3]_2$, $\eta^5\text{-}C_5H_5M(CO)_3I$ (M = Mo, W) AND ISONITRILES

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(Received March 18th, 1981)

Summary

The reaction between $\eta^5\text{-}C_5H_5M(CO)_3I$ (M = Mo, W) and isonitriles, RNC, (RNC = $PhCH_2NC$, t-BuNC and 2,6-dimethylphenylisocyanide (XyNC)) is catalysed by the dimer $[\eta^5\text{-}C_5H_5M(CO)_3]_2$ (M = Mo, W) to yield $\eta^5\text{-}C_5H_5M(CO)_{3-n}(RNC)_nI$ (n = 1—3) and $[\eta^5\text{-}C_5H_5Mo(RNC)_4]I$. The complexes $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(RNC)_n$ (n = 1, RNC = MeNC, $PhCH_2NC$, XyNC, t-BuNC; n = 2, RNC = t-BuNC) have been prepared in moderate yield from the direct reaction between $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ and RNC, and also catalyse the above reaction. A reaction pathway involving a fast non-chain radical mechanism and a slower chain radical mechanism is proposed to account for the catalysed reaction.

Introduction

Organometallic compounds containing the isonitrile ligand (RNC) have been known for many years and synthetic routes to these complexes have been well documented [1—3]. In many instances preparative routes to the metal-isonitrile complexes, specifically to metals in low oxidation states containing more than one RNC ligand, lead to the required products in low yield, if at all [4]. Our investigations into the use of catalysts in the synthesis of metal-isonitrile complexes have allowed us easy access to many complexes of the above type and at the same time enabled us to explore mechanistic features of the substitution reactions involving the RNC ligand [5,6].

Herein we report our results on the CO substitution reaction of $\eta^5\text{-}C_5H_5Mo(CO)_3I$ (I), and $\eta^5\text{-}C_5H_5W(CO)_3I$, (II) by RNC in the presence of a catalyst [7]. It has previously been shown that complete and partial CO substitution of $\eta^5\text{-}C_5H_5Mo(CO)_3X$ (X = Cl, Br) by RNC to give $\eta^5\text{-}C_5H_5Mo(CO)_{3-n}(RNC)_nX$ (n = 1, 2) and $[\eta^5\text{-}C_5H_5Mo(RNC)_4]X$ can be achieved [8—10], but that reaction of RNC with I yields only the mono-substituted derivative $\eta^5\text{-}C_5H_5Mo$-

0022-328X/81/0000—0000/$02.50

$(CO)_2(RNC)I$ (RNC = t-BuNC, [9], PhNC [10] and MeNC [11]).

The catalyst initially used in this study was either $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ (III) or $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ (IV) as it was anticipated that the reaction would occur via a free radical chain mechanism [12], as was originally proposed [7]. Our recent findings that a non-chain radical mechanism could account for the catalysed reaction between $\eta^5\text{-}C_5H_5Fe(CO)_2I$ and RNC [5] necessitated a reassessment of our earlier proposal. Thus, the complexes $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(RNC)_n$ ($n = 1, 2$) were synthesised for use as catalysts for the reaction between I and RNC. These complexes were prepared from the direct reaction between RNC and III but using a modification of the literature method [11] which gave a reported yield of only 1% (RNC = MeNC). Our modified route gave yields of between 30—50%.

The combined results on the use of III, IV and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(RNC)_n$ ($n = 1, 2$) as CO substitution catalysts are reported herein.

Experimental

$[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ (I), and $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ were purchased from Strem Chemicals. $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ (II) [13], $\eta^5\text{-}C_5H_5Mo(CO)_3I$ (III) [9] and $\eta^5\text{-}C_5H_5W(CO)_3I$ (IV) [14] were prepared by literature methods. The isonitriles were purchased from Fluka A.G. (t-BuNC and 2,6-dimethylphenylisocyanide (XyNC)), from Aldrich ($PhCH_2NC$) or prepared by the method of Casanova et al. [15] (MeNC).

IR spectra (Table 1) were recorded on a JASCO IRA-1 spectrometer, NMR data (Table 3) on a Bruker WP80 FTNMR Spectrometer and mass spectra on a Varian Mat CH5 spectrometer operating at 70 eV. Melting points were recorded on a Koffler hot stage apparatus and are uncorrected. Microanalyses were performed by the Microanalytical Laboratories, C.S.I.R. and are reported in Table 1.

Benzene was distilled from sodium-benzophenone under nitrogen and all reactions were routinely carried out under a nitrogen atmosphere.

Column chromatography was carried out with silica gel (Merck, Kieselgel 80).

Preparation of $\eta^5\text{-}C_5H_5Mo(CO)_2(RNC)I$ *(RNC = t-BuNC, XyNC,* $PhCH_2NC$*)*

I (1 mmol) and III (10 mg; 0.02 mmol) were added to benzene (15 ml) and the solution heated in an oil bath pre-set at 90°C. RNC (1 mmol) was then added to the hot, stirred solution and the course of the reaction monitored by IR spectroscopy. Typically the reaction was complete <30 min. At the end of the reaction the solution was reduced to 5 ml on a rotary evaporator and then added to a silica gel column (previously washed with hexane). Elution of the column with hexane (100 ml) and finally a 2/3 benzene/hexane mixture gave the required complex as a mixture of two isomers (vide infra). Solvent was removed and the product obtained in yields of 50—80% (Table 1). Recrystallisation was achieved from CH_2Cl_2/hexane mixtures.

Preparation of $\eta^5\text{-}C_5H_5W(CO)_2(RNC)I$ *(RNC = t-BuNC, XyNC)*

II (1 mmol) and IV (15 mg, ~0.02 mmol) were added to benzene (15 ml)

TABLE 1

PREPARATIVE AND ANALYTICAL DATA FOR THE ISONITRILE COMPLEXES

	Reaction time (min)	Yield (%)	M.p. (°C)	Analyses (Found (calcd.) (%))			Mol. mass [a]
				C	H	N	
η^5-$C_5H_5Mo(CO)_2$(t-BuNC)I [b]	30	70	156—157	33.85 (33.75)	3.22 (3.30)	3.25 (3.28)	429
η^5-$C_5H_5Mo(CO)_2$(XyNC)I	15	74	132—140	40.28 (40.44)	3.03 (2.97)	2.93 (2.95)	477
η^5-$C_5H_5Mo(CO)_2(PhCN_2NC)I$	30	80	94—98	39.00 (39.07)	2.70 (2.62)	3.10 (3.04)	463
η^5-$C_5H_5W(CO)_2$(t-BuNC)I	45	60	93—94	28.03 (28.89)	2.64 (2.83)	2.78 (2.71)	515
η^5-$C_5H_5W(CO)_2$(XyNC)I	60	65	~120	34.80 (34.13)	2.50 (2.51)	2.50 (2.49)	563
η^5-$C_5H_5Mo(CO)$(t-BuNC)$_2$I [d]	10	60	c	39.25 (39.85)	4.60 (4.80)	5.76 (5.80)	484
η^5-$C_5H_5Mo(CO)$(XyNC)$_2$I [d]	2	65	123—127	50.51 (49.84)	4.15 (4.00)	4.94 (4.84)	580
η^5-$C_5H_5Mo(CO)(PhCH_2NC)_2I$ [d]	20	50	~100	48.18 (48.02)	3.40 (3.48)	5.01 (5.09)	552
[η^5-C_5H_5Mo(t-BuNC)$_4$]I	360	40	c	46.22 (48.39)	5.16 (6.66)	8.11 (9.03)	—
[η^5-C_5H_5Mo(XyNC)$_4$]PF_6	45	70	162—165	57.94 (59.28)	4.86 (4.98)	6.73 (6.75)	—
(η^5-$C_5H_5)_2Mo_2(CO)_5$(t-BuNC)	e	30	c	44.44 (44.06)	3.56 (3.50)	2.62 (2.57)	549
(η^5-$C_5H_5)_2Mo_2(CO)_5$(XyNC)	e	30	c	48.73 (48.59)	3.41 (3.23)	2.42 (2.36)	597
(η^5-$C_5H_5)_2Mo_2(CO)_5(PhCH_2NC)$	e	45	125—127	47.96 (47.69)	3.02 (2.96)	2.42 (2.42)	583
(η^5-$C_5H_5)_2Mo_2(CO)_5$(MeNC) [f]	e	50	~150	40.66 (40.65)	2.79 (2.60)	2.68 (2.78)	—
(η^5-$C_5H_5)_2Mo_2(CO)_4$(t-BuNC)$_2$	e	45	~145	47.65 (48.01)	4.70 (4.70)	4.82 (4.67)	604

[a] Obtained from mass spectra using ^{98}Mo and ^{184}W,isotopes. [b] See also [9]. [c] Ill defined. [d] Reaction time for preparation of complex refers to time taken for synthesis from the mono-substituted derivative; see experimental. [e] See experimental. [f] See also [11].

TABLE 2

IR DATA [a, b]

	ν(NC)	ν(CO)
η^5-$C_5H_5W(CO)_2$(XyNC)I	2110	1963, 1908, 1901
η^5-$C_5H_5W(CO)$(XyNC)$_2$I	2095, 2046, 1998	1894, 1872
η^5-C_5H_5Mo(t-BuNC)$_3$I	2085, 2015	—
[η^5-C_5H_5Mo(XyNC)$_4$]PF_6 [c]	2144, 2074, 1997	—
[η^5-C_5H_5Mo(t-BuNC)$_4$]I [c]	2150, 2090, 2045	—
(η^5-$C_5H_5)_2Mo_2(CO)_5$(t-BuNC)	2114	1966, 1917, 1887
(η^5-$C_5H_5)_2Mo_2(CO)_5$(XyNC)	2075	1960, 1920, 1893
(η^5-$C_5H_5)_2Mo_2(CO)_5(PhCH_2NC)$	2118	1969, 1917, 1889
(η^5-$C_5H_5)_2Mo_2(CO)_5$(MeNC)	2137	1972, 1916, 1889
(η^5-$C_5H_5)_2Mo_2(CO)_4$(t-BuNC)$_2$	2110, 2035	1940, 1920, 1885, 1866
η^5-$C_5H_5Mo(CO)_2(PPb_3)I$ [d]	—	1963, 1889, 1873

[a] in C_6D_6 solution (cm^{-1}) unless otherwise stated. [b] The IR data on the other isonitrile derivetives can be found in [7]. [c] Recorded in $CDCl_3$ solution. [d] See also [16].

TABLE 3

NMR DATA [a, b]

	C_5H_5 [c]		CH_2 or CH_3 [c]		Ph
	A or C	B or D	A or C	B or D	
η^5-$C_5H_5Mo(CO)_2$(t-BuNC)I	4.83	4.79	0.85	0.98	—
η^5-$C_5H_5Mo(CO)_2$(XyNC)I	4.80	4.78	2.21	1.92	6.61
η^5-$C_5H_5Mo(CO)_2(PhCH_2NC)I$	4.79	4.75	4.10	3.94	7.02
η^5-$C_5H_5W(CO)_2$(t-BuNC)I	4.82	4.74	1.01	0.90	—
η^5-$C_5H_5W(CO)_2$(XyNC)I	4.87	4.82	2.27	1.98	6.68
η^5-$C_5H_5Mo(CO)$(t-BuNC)$_2$I	5.03	5.00	1.11	1.15 1.11	
η^5-$C_5H_5Mo(CO)(XyNC)_2I$	5.10	5.09	2.41	2.27 2.08	6.7
η^5-$C_5H_5Mo(CO)(PhCH_2NC)_2I$	4.92	4.92	4.31	4.36 4.24	6.9
η^5-$C_5H_5W(CO)$(t-BuNC)$_2$I	5.03	4.97	1.13	1.18 1.15	—
η^5-$C_5H_5W(CO)(XyNC)_2I$	5.16	5.10	2.44	2.30 2.12	6.72
η^5-C_5H_5Mo(t-BuNC)$_3$I	4.94		1.26	1.26	—
η^5-$C_5H_5Mo(XyNC)_3I$ [d]	5.15		2.34	2.11	6.70
[η^5-C_5H_5Mo(t-BuNC)$_4$]I [e]	5.08		1.53		—
[η^5-$C_5H_5Mo(XyNC)_4]PF_6$ [e]	5.54		2.28		7.04
$(\eta^5$-$C_5H_5)_2Mo_2(CO)_5$(t-BuNC)	4.93, 4.88 [f]		1.03		—
$(\eta^5$-$C_5H_5)_2Mo_2(CO)_5(XyNC)$	4.93		2.19		6.7
$(\eta^5$-$C_5H_5)_2Mo_2(CO)_5(PhCH_2NC)$	4.91		4.10		7.1
$(\eta^5$-$C_5H_5)_2Mo_2(CO)_5(MeNC)$	4.91		2.31		—
$(\eta^5$-$C_5H_5)_2Mo_2(CO)_4$(t-BuNC)$_2$ [g]	5.13, 5.02, 4.96		1.22, 1.12		—
η^5-$C_5H_5Mo(CO)_2(PPh_3)I$ [e, h]	5.12	4.86 [i]	—		7.2

[a] In C_6D_6 solution unless otherwise stated. [b] Chemical shifts in ppm downfield from internal TMS. [c] A, B, C, D, refer to isomers; see Fig. 1 and text for explanation. [d] Ratio of CH_3 peaks, 2/1. [e] Recorded in $CDCl_3$ solution. [f] Data refer to *cis—trans* isomers (see text). [g] Data refer to conformers (see text). [h] See also [16]. [i] doublet, *J* 2 Hz.

and the solution heated in an oil bath pre-set at 90°C. Addition of RNC (1 mmol) to the hot, stirred solution then followed and the reaction was monitored by following changes in the ν(CO) region of the IR spectrum. The reaction was complete in <45 min. Product work-up was identical to that described for the molybdenum reaction. Yields were typically 60—65% (Table 1). Recrystallisation was achieved from CH_2Cl_2/hexane mixtures.

Preparation of η^5-$C_5H_5Mo(CO)(RNC)_2I$ (RNC = t-BuNC, XyNC, $PhCH_2NC$)

I (1 mmol) and III (10 mg, 0.02 mmol) were added to benzene (15 ml) and the solution heated in an oil bath pre-set at 90°C. RNC (1 mmol) was then added to this hot stirred solution and the reaction monitored by IR spectroscopy. After I had been consumed (or the IR spectrum indicated no further product formation) a second equivalent of RNC (1 mmol) was added to the reaction solution. The reaction was again monitored by IR spectroscopy. Reaction times for the synthesis of η^5-$C_5H_5Mo(CO)(RNC)_2I$ from η^5-$C_5H_5Mo(CO)_2(RNC)I$, prepared in situ, and RNC are given in Table 1. At the end of the reaction the solvent was reduced to 5 ml on a vacuum pump and the solution then added to a silica column previously washed with dry, degassed hexane. The column was eluted with dry, degassed solvents, firstly hexane and then benzene, and the required product was collected under nitrogen. No attempt was made to separate the two isomers (vide infra) which were eluted. The required product was crystallised from CH_2Cl_2 and hexane.

Preparation of η^5-$C_5H_5W(CO)(RNC)_2I$ (RNC = t-BuNC, XyNC)

II (1 mmol) and IV (15 mg, 0.02 mmol) were added to benzene (15 ml) and the solution brought to reflux. RNC (1 mmol) was then added, and the reaction followed by IR spectroscopy. After II had been consumed (or no further product formation could be detected in the IR spectrum) a second equivalent of RNC (1 mmol) was added to the reaction solution. The reaction was again monitored by IR spectroscopy and continued until all the η^5-$C_5H_5W(CO)_3$-(RNC)I, produced in situ, had been consumed. The solution was then filtered under nitrogen and the product crystallized from benzene/hexane mixtures. The facile decomposition of these complexes on silica (or alumina) columns precludes their separation by chromatographic procedures.

Preparation of η^5-$C_5H_5Mo(XyNC)_3I$

Stepwise addition of XyNC (3 × 1 mmol) to a stirred refluxing benzene solution (15 ml) containing I (1 mmol) and III (10 mg, 0.02 mmol) was followed by IR spectroscopy. During the addition the reaction solution went from red to deep red to black. At the end of the reaction all the η^5-$C_5H_5Mo(CO)(XyNC)_2I$, produced in situ, had been consumed. The reaction mixture was filtered under nitrogen and the product obtained as black air sensitive crystals (m.p. 138—142° C). The product was characterized by IR, NMR (Table 3) and mass spectra (parent ion 683).

Preparation of $(\eta^5$-$C_5H_5)_2Mo_2(CO)_5RNC$ (RNC = t-BuNC, $PhCH_2NC$, XyNC, MeNC) and $(\eta^5$-$C_5H_5)_2Mo_2(CO)_4(t$-$BuNC)_2$

III (500 mg, 1 mmol) was added to benzene (10 ml) and the solution heated in an oil bath pre-set at 90° C. Slow addition of a dilute benzene solution of RNC (40 μl/ml benzene) to the vigorously stirred solution over a period of 90—120 min was monitored by removing small portions of the reaction mixture and eluting this mixture on TLC plates (hexane/benzene 2/3). During this time III was consumed and the new products could be detected on the TLC plates. At the end of the reaction the mixture was cooled, solvent reduced to ~5 ml and the mixture placed on top of a silica column previously washed with dry, degassed hexane. The column was then eluted with dry degassed solvents (hexane and then hexane/benzene mixtures). The red products were collected under nitrogen and were recrystallised from benzene/hexane.

Preparation of $[\eta^5$-$C_5H_5Mo(t$-$BuNC)_4]I$

I (1 mmol) and $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ (10 mg, ~0.02 mmol) were added to benzene (10 ml) and the solution heated in an oil bath pre-set at 90° C. Three equivalents of t-BuNC (3 mmol) were then added stepwise to the reaction solution. Addition of the first two equivalents resulted in formation of η^5-$C_5H_5Mo(CO)$-$(t$-$BuNC)_2I$ in ~40 min. Further reaction proceeded slowly (~120 min) during which time the reaction solution darkened and an orange precipitate deposited. The solution was cooled and filtered through a cellulose column (under nitrogen). Solvent was removed from the filtrate to yield a dark purple complex, believed to be η^5-$C_5H_5Mo(t\text{-}BuNC)_3I$ (vide infra). The cellulose column was washed with further portions of benzene and then finally with CH_2Cl_2 to yield an orange solution. Addition of hexane to the orange CH_2Cl_2 solution gave an orange product characterised as $[\eta^5$-$C_5H_5Mo(t\text{-}BuNC)_4]I$ (Table 1).

Preparation of $[\eta^5$-$C_5H_5Mo(XyNC)_4]PF_6$

XyNC (4 mmol) was added to III (1 mmol) in refluxing benzene (20 ml) and the reaction monitored by IR spectroscopy. At the end of the reaction (~45 min) solvent was removed and the reaction mixture redissolved in ethanol (10 ml) and filtered. To the filtrate was added excess $NaPF_6$ in ethanol (5 ml). The solution, together with 10 ml water, was then heated on a water bath and the required product crystallised out as orange needles in good yield (70%).

Preparation of η^5-$C_5H_5Mo(CO)_2(PPh_3)I$

I (1 mmol), PPh_3 (1 mmol) and III (10 mg, 0.02 mmol) were added to benzene (15 ml) and the solution refluxed in an oil bath. The reaction was followed by IR spectroscopy and was complete <45 min. The product was purified by column chromatography and recrystallised from a CH_2Cl_2/hexane mixture.

Discussion

The reaction between I or II and RNC (equimolar) in refluxing benzene is slow and even after long reaction times yields are ~30% [9—11]. However, addition of small quantities (~2% mol ratio) of dimer III or IV to the above solutions brings about a dramatic increase in reaction rate (Table 1). The reaction can readily be followed by either changes in the IR spectra (ν(CO) region) or by observing product formation on TLC plates (silica gel; benzene/hexane as eluent). The TLC plates indicate that two complexes with similar R_f values are formed in the reaction. The complex with higher R_f value is orange whereas the other complex is pink. They are the two isomers, A and B (Fig. 1), of the required complex η^5-$C_5H_5M(CO)(RNC)I$ [9] (vide infra), but no attempt was

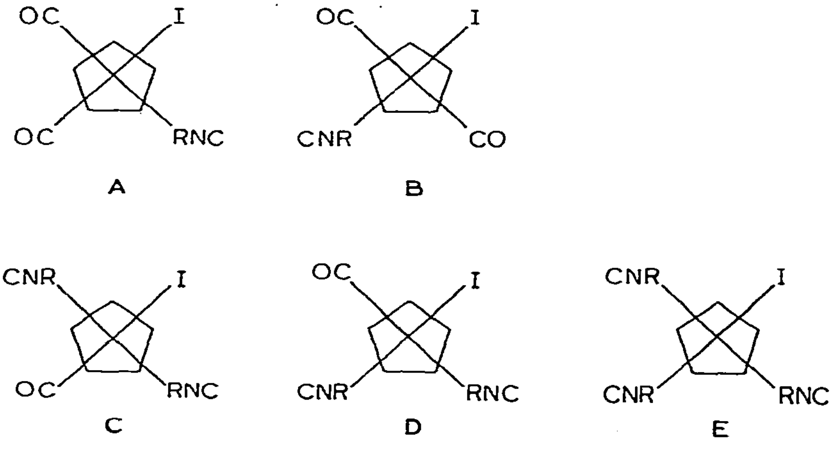

Fig. 1. Newman projections of the isonitrile complexes η^5-$C_5H_5Mo(CO)_{3-n}(RNC)_nI$ (n = 1—3).

made to separate these isomers. The reactions are quite specific and only a low yield (<5%) of the disubstituted product was obtained. The disubstituted product (together with catalyst) can readily be removed from the required complex by elution of the reaction material through a silica-gel column.

The disubstituted products, η^5-$C_5H_5M(CO)(RNC)_2I$, were prepared by stepwise addition of 2 equivalents of RNC to I or II and catalyst. Again, the reaction can readily be monitored by IR spectroscopy. Interestingly, the second equivalent substitutes onto the reactant more rapidly than the first equivalent (Table 1) e.g. addition of the first equivalent of XyNC to I gives a slow reaction (~15 min) whereas vigorous CO evolution occurs on addition of the second equivalent of XyNC.

As expected, two isomers of the required product (C and D, Fig. 1) were detected on TLC plates, but no attempt was made to separate the isomers.

Attempts to prepare η^5-$C_5H_5Mo(RNC)_3I$ derivatives were made. Addition of XyNC to III and η^5-$C_5H_5Mo(CO)(XyNC)_2I$ (prepared in situ) resulted in CO evolution and a darkening of the solution. Changes in the IR spectrum indicated that the required product, η^5-$C_5H_5Mo(XyNC)_3I$, had been prepared. Although we were unable to obtain satisfactory elemental analyses for this complex all other physical data are in accordance with its formulation (vide infra). An attempt to prepare η^5-$C_5H_5Mo(t\text{-}BuNC)_3I$ as above resulted in minor changes in the IR spectrum consistent with product formation. However, under these conditions the catalyst tends to react with t-BuNC to give salts. The use of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ as catalyst did result in a slow reaction between I and t-BuNC to give the air-sensitive complex η^5-$C_5H_5Mo(t\text{-}BuNC)_3I$ (low yield) as well as an orange crystalline precipitate, characterized as $[\eta^5\text{-}C_5H_5Mo(t\text{-}BuNC)_4]I$ [9]. $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ does not form salts in the presence of excess RNC.

The stability of the complexes decreased on RNC substitution and the molybdenum complexes are more stable than the tungsten complexes. (The η^5-$C_5H_5W(CO)(RNC)_2I$ complexes decompose on silica-gel columns even when dry, degassed solvents are used).

Addition of an equivalent of XyNC to the reaction mixture containing η^5-$C_5H_5Mo(XyNC)_3I$ and III resulted in the black solution turning yellow as $[\eta^5\text{-}C_5H_5Mo(XyNC)_4]I$ was formed. The displacement of I from molybdenum by RNC is a much slower reaction than the displacement of the CO groups.

The following reactions were also performed but products were characterized only by IR spectroscopy.

$$\text{(a) } \eta^5\text{-}C_5H_5Mo(CO)_3I + n\text{ XyNC } (n = 1\text{—}4) \xrightarrow{[\eta^5\text{-}C_5H_5Fe(CO)_2]_2}$$

$$\eta^5\text{-}C_5H_5Mo(CO)_{3-n}(XyNC)_nI\ (n = 1\text{—}3) \text{ and } [\eta^5\text{-}C_5H_5Mo(XyNC)_4]I$$

(addition of the first three equivalents required ~2 min per equivalent for complete reaction; conversion to the salt required ~45 min).

$$\text{(b) } \eta^5\text{-}C_5H_5W(CO)_3I + n(XyNC)\ (n = 1, 2)$$

$$\xrightarrow{\text{III}} \eta^5\text{-}C_5H_5W(CO)_{3-n}(XyNC)_nI\ (n = 1, 2)$$

To elucidate the mechanism of the above reaction it was found necessary to prepare the complexes $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(RNC)_n$ ($n = 1, 2$). A modification of the direct reaction between RNC and II [11] i.e. a slow dropwise addition of a dilute solution of RNC to II in refluxing benzene gave the required products in moderate yield. This modified procedure was necessary to reduce salt formation, $[\eta^5\text{-}C_5H_5Mo(RNC)_4][\eta^5\text{-}C_5H_5Mo(CO)_3]$, which occurs when II and excess RNC are allowed to react together [9]. Indeed, we found that if XyNC (1 equivalent) is added to III in refluxing benzene without dilution then ~20% salt is formed with only minor amount of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(XyNC)$ being detected. Addition of 4 equivalents of XyNC gives the salt in high yield.

The slow addition of RNC to III was followed by TLC plates and during the reaction new complexes could readily be detected. For RNC = t-BuNC two red complexes (as well as salt) could be detected. These could be separated by column chromatography and characterization by IR, NMR and mass spectra revealed that they were $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(\text{t-BuNC})$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\text{t-BuNC})_2$. For the other isonitriles it was only possible to isolate the mono-substituted derivative although TLC indicated the presence of another red complex, presumed to be the di-substituted derivative, which was unstable TLC plates. The new complexes are red and are stable indefinitely in the solid state.

Product characterization

Product characterization was achieved by a combination of IR, mass and NMR spectroscopy. I can be regarded as having a piano-stool configuration [17] and substitution of one CO group by RNC can thus result in isomer formation (A and B, Fig. 1). An X-ray structure determination of $\eta^5\text{-}C_5H_5Mo(CO)_2(PhNC)I$ (isomer B) [18] has confirmed the piano-stool arrangement for these complexes.

The existence of both isomers (A and B) in all the reaction mixtures has been detected by IR and NMR spectroscopy, and TLC. NMR spectra recorded in either $CDCl_3$ or C_6D_6 (Table 3) indicate two cyclopentadienyl resonances and two resonances for either the CH_2 or CH_3 portion of the RNC ligand (where applicable). In accordance with earlier studies [9,19] we have assigned the low field C_5H_5 resonance as due to isomer A. Freshly prepared solutions of $\eta^5\text{-}C_5H_5Mo(CO)_2(RNC)I$ (RNC = XyNC, $PhCH_2NC$) indicate the ratio of A/B to be in the range 2/1. For RNC = t-BuNC freshly prepared solutions reveal the presence of ~90% of the B isomer [9]. If the solution is warmed to 80°C for a few minutes interconversion to an A/B ratio of ~2/1 then occurs. Presumably the bulky t-BuNC ligand has difficulty in rearranging its position within the metal coordination sphere. The interconversion of corresponding isomers for the $\eta^5\text{-}C_5H_5Mo(CO)_2(PR_3)I$ complexes has been studied in some detail [17] and this same interconversion process is believed to apply to the isonitrile derivatives. This is supported by the NMR spectrum of $\eta^5\text{-}C_5H_5Mo(CO)_2(PhCH_2NC)I$ which gives only two resonances of unequal intensity for the CH_2 protons. This suggests that at ~25°C isomers A and B interchange more slowly than the environment of the H atoms of the methylene protons (otherwise a doublet for the CH_2 protons, isomer A, would have been observed).

The IR spectra (2100—1800 cm^{-1}) of the $\eta^5\text{-}C_5H_5Mo(CO)_2(RNC)I$ complexes have also been recorded in both $CDCl_3$ and C_6D_6 (Table 2 and ref. 7). In general the spectrum consists of a band of medium intensity at ~2100 cm^{-1} (ν(NC)) and either one broad band at ~1920 cm^{-1} ($CDCl_3$) or two bands at ~1920 and 1910 cm^{-1} (C_6D_6) (ν(CO)). These data are consistent with the existence of two isomers; isomers A (2100, 1980, 1910 cm^{-1}) and B (2100, 1980, 1920 cm^{-1}). Further confirmation is supplied by the IR spectrum of η^5-C_5H_5-$Mo(CO)_2$(t-BuNC)I. When initially prepared the complex has absorption bands at 2138, 1973 and 1915 cm^{-1} but after heating at 80° C this changes to four bands at 2138, 1973, 1915 and 1902 cm^{-1}. Taken together with the NMR data this implies that the absorption band (asymmetric ν(CO) stretch) at 1902 cm^{-1} must be associated with isomer A [11] and at 1915 cm^{-1} with isomer B.

The disubstituted derivatives can also be expected to exist as a mixture of two isomers (C and D, Fig. 1). NMR, IR and TLC confirm this prediction. NMR data recorded in $CDCl_3$ or C_6D_6 (Table 3) show in general two resonances for the η^5-C_5H_5 group and one strong and two weak absorptions (of equal intensity) for the CH_2 or CH_3 portion of the RNC ligand, where applicable (Table 3). A consideration of Fig. 1 (RNC = XyNC) reveals that isomer C would be expected to have one CH_3 resonance while isomer D with two non-equivalent RNC groups would have two resonances of equal intensity. No evidence has been detected in the NMR spectra for restricted rotation of the RNC ligand around its own axis (ambient temperature) e.g. at lower temperatures non-equivalence of all four of the CH_3 groups of the XyNC ligands in η^5-C_5H_5Mo(CO)-$(XyNC)_2$I (isomer D) would be predicted. The presence of only two proton resonances (isomer D) and one proton resonance (isomer C) for CH_2 in η^5-C_5H_5-Mo(CO)$(PhCH_2NC)_2$I again implies that isomer C—isomer D interchange is slower than interchange of the environment of the methylene protons [17].

The IR spectra recorded in $CDCl_3$ and C_6D_6 (Table 2 and ref. [7]) are also in accord with isomer formation. The ν(NC) region (2100—2000 cm^{-1}) in both solvents consists of one strong band flanked by one or two weak bands. In $CDCl_3$ only one broad ν(CO) resonance is detected but this is resolved into two absorptions in C_6D_6. The two absorptions are a direct consequence of the CO ligand being *trans* to the iodide or isonitrile ligand (isomers C and D).

The trisubstituted derivatives η^5-C_5H_5Mo$(RNC)_3$I can only exist in one isomeric form (E, Fig. 1). This is confirmed by the NMR spectrum (RNC = XyNC, Table 3) which shows one C_5H_5 resonance, and two CH_3 resonances in a 2/1 ratio due to the two types of XyNC ligands. The IR spectrum confirms the presence of isonitrile ligands and lack of CO ligands.

All the above compounds were further characterized by mass spectra. In every case a parent ion as well as fragment ions corresponding to loss of CO and RNC were detected. The complex η^5-C_5H_5Mo$(XyNC)_3$I was further characterized by the presence of numerous $(m/e)^{2+}$ ions e.g. $[\eta^5$-$C_5H_5Mo(XyNC)_3]^{2+}$, $[\eta^5$-$C_5H_5Mo(XyNC)_2I]^{2+}$, and $[\eta^5$-$C_5H_5Mo(XyNC)I]^{2+}$.

The products obtained from the reaction of RNC with III also showed simple NMR spectra. Thus, only a broad resonance for the C_5H_5 ligand and the CH_2 or CH_3 portion of the RNC ligand (where applicable) were detected at ambient temperature. Cotton et al. [11] have studied the variable temperature NMR spectra of $(\eta^5$-$C_5H_5)Mo_2(CO)_5$(MeNC) in detail and have shown that at room temperature the CO and MeNC are fluxional. Our results for RNC = $PhCH_2NC$, and XyNC are in accord with this finding. The NMR spectra of

$(\eta^3\text{-}C_5H_5)_2Mo_2(CO)_{6-n}(\text{t-BuNC})_n$ ($n = 1, 2$) are more complex and suggest that different conformers or isomers could be frozen out at this temperature. For $n = 1$, two C_5H_5 resonances of unequal intensity together with one broadened CH_3 resonance are observed in the NMR spectrum ($CDCl_3$ or C_6D_6). The most likely explanation is that *cis* and *trans* isomers are interconverting more slowly than the isonitrile ligand is exchanging between the two metal atoms [11]. For $n = 2$ a more complex spectrum consisting of 3 unequal C_5H_5 resonances and two CH_3 resonances is observed. A variable temperature NMR study will be needed to elucidate and interpret this spectrum.

The IR spectra of all the new dimer complexes were recorded in $CHCl_3$ and C_6D_6 (Table 2). The complexes $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(RNC)$ all show 4 bands in the 2200—1850 cm^{-1} region; a medium band at ~2100 cm^{-1} (ν(NC)) and three bands, usually strong, between 2000—1850 cm^{-1} (ν(CO)). In cyclohexane a more complicated spectrum is obtained [11]. The IR spectrum of $(\eta^5\text{-}C_5H_5)_2$-$Mo_2(CO)_4(\text{t-BuNC})_2$ consists of one strong band (1886 cm^{-1}, ν(CO)) and a number of weaker bands (Table 2) consistent with the spectra recorded for the analogous phosphine and phosphite derivatives [20]. This would imply that this complex exists, at least, as a mixture of *cis* and *trans* isomers [21] in C_6D_6.

Mass spectra were also used to characterize these complexes. All the complexes revealed similar mass spectroscopic fragmentation patterns: parent ion, stepwise loss of CO and finally loss of RNC. Doubly charged ions also aided the structure determination.

Finally, the salts, $[\eta^5\text{-}C_5H_5Mo(RNC)_4]I$, were readily characterized by their NMR spectra (one C_5H_5 absorption and one RNC absorption; in the correct intensity ratio), elemental analyses and IR spectra.

Reaction mechanism

III and IV and other related dimer species are known to dissociate into 17 electron radicals under appropriate conditions (thermal, photochemical) [22]. To confirm the presence of radicals in our own reaction, we have carried out a number of experiments and relevant results and observations are reported below (see also [7]).

(1) The synthesis of $\eta^5\text{-}C_5H_5Mo(CO)_2(RNC)I$, by addition of catalytic amounts of III to I and RNC, gives erratic results; in some instances long inhibition times were observed.

(2) The above reaction is light sensitive. Irradiation with a 500 watt light bulb gives a dramatic increase in the reaction rate. There is even a detectable rate change on carrying out the reaction in the dark (flask wrapped in aluminium foil) as compared to carrying out the reaction without any precaution to exclude visible light.

(3) The above reaction typically takes <30 min and is dependent on the nature of the isonitrile (Table 1).

(4) The reaction between I and PPh_3 is catalysed by III and gives the expected product $\eta^5\text{-}C_5H_5Mo(CO)_2(PPh_3)I$ in ~120 min. No catalysis was observed for the reaction with $SbPh_3$. The catalytic reaction is hence not dependent on the presence of RNC but the reaction rate is again dependent on the nature of the incoming ligand.

(5) The rate of the reaction between I and t-BuNC to give $\eta^5\text{-}C_5H_5Mo(CO)_2$-

(t-BuNC)I is dependent on the nature of the catalyst used viz. $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2 > [\eta^5\text{-}C_5H_5Mo(CO)_2]_2 > [\eta^5\text{-}C_5H_5W(CO)_2]_2$ which corresponds to the metal—metal bond strength of the catalyst.

(6) A 0.5/1/1 reaction carried out between catalyst/I/t-BuNC gives the following rate sequence for the catalysts: $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\text{t-BuNC})_2 >$ $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(\text{t-BuNC}) >$ III (benzene, 67°C). This sequence can be rationalised by the ability of the t-BuNC ligand to facilitate radical formation, from the dimer species, as has been found previously [5].

The effect of radical inhibitors is shown by the following results:

(7) A 0.5/1/1 reaction of III/I/t-BuNC at 67°C (benzene) gives a complete reaction to give $\eta^5\text{-}C_5H_5Mo(CO)_2(\text{t-BuNC})I$ in <20 min as detected by IR spectroscopy.

(8) A 0.5/1/1 reaction of III/I/t-BuNC and 1 equivalent of the radical inhibitor, hydroquinone, results in a slower reaction rate (~80 min). Although one equivalent of hydroquinone was added the effective concentration is very low as hydroquinone is not particularly soluble in benzene.

(9) A 0.5/1/1 reaction of III/I/t-BuNC and the radical inhibitor galvinoxyl (10% by mol. mass) results in a reduced reaction rate (~120 min; 90% completion).

The above results all suggest that radicals are implicated in the reaction mechanism. The first step in the reaction can thus be envisaged as:

$$[\eta^5\text{-}C_5H_5Mo(CO)_3]_2 \overset{\Delta \text{ or } h\nu}{\rightleftharpoons} \eta^5\text{-}C_5H_5Mo(CO)_3^{\cdot}$$

Following formation of the radical there are two possible mechanisms by which the radical can act as a catalyst: (i) a non-chain radical pathway as outlined for the substitution reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2I$ [5] or (ii) a radical chain mechanism in which the radical initally undergoes rapid substitution by RNC in an associative [23] or dissociative [24] step viz.:

$$\eta^5\text{-}C_5H_5Mo(CO)_3^{\cdot} + RNC \rightarrow \eta^5\text{-}C_5H_5Mo(CO)_2RNC^{\cdot} + CO$$

The catalytic cycle is then completed by halide exchange between $\eta^5\text{-}C_5H_5Mo(CO)_2RNC^{\cdot}$ and I.

We believe that both processes are occurring simultaneously, but at different rates. Thus, for the synthesis of $\eta^5\text{-}C_5H_5Mo(CO)_2(\text{t-BuNC})I$:

(10) A 0.5/1/1 reaction carried out between $(\eta^5\text{-}C_5H_5)Mo_2(CO)_5(\text{t-BuNC})$/I/t-BuNC occurs at ~six times the rate as a reaction carried out between a 0.5/1 mixture of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5(\text{t-BuNC})$ and I (benzene, 67°C). This implies that attack from uncoordinated t-BuNC is faster than dimer dissociation and halide exchange in generating the reaction product. However, both reactions are occurring at this temperature.

(11) The reaction between a 0.5/1/1 mixture of III/I/t-BuNC (benzene, 56°C) yields $\eta^5\text{-}C_5H_5Mo(CO)_2(\text{t-BuNC})I$ and was virtually complete in <90 min. The corresponding reaction between III and t-BuNC gave little, if any, product during the same time interval (IR spectra, odour of RNC); at reflux (~78°C) salt formation is rapid (<5 min). This suggests that the reaction between $\eta^5\text{-}C_5H_5Mo(CO)_3^{\cdot}$ and t-BuNC is slow at 56°C relative to the formation of $\eta^5\text{-}C_5H_5Mo(CO)_2(\text{t-BuNC})I$.

(12) When the experiments listed in (11) are carried out while being irradiated (500 watt light bulb) both reactions are complete in minutes (benzene, 71°C).

The non-chain component of the reaction is further highlighted by the following reactions:

(13) A 0.5/1/1 reaction between $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$/I/t-BuNC in benzene (45°C) gave $\eta^5\text{-}C_5H_5Mo(CO)_2(t\text{-}BuNC)I$ (>90%) in 5 h.

(14) A 1/1 reaction between $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(t\text{-}BuNC)$ [5] and I in benzene (45°C) did not give a reaction in 5 h.

(16) The reaction between $\eta^5\text{-}C_5H_5Mo(XyNC)_3I$ and XyNC is catalysed by III and gives the salt $[\eta^5\text{-}C_5H_5Mo(XyNC)_4]I$.

The above data, taken together, are consistent with the chain mechanism [5] occurring at a faster rate than the non-chain mechanism [7] but that both mechanisms must be occurring simultaneously (cf. specifically experiment (10)). Our results are at variance with the generally accepted view [12,24] that radicals react rapidly with nucleophiles e.g. PR_3. Present studies are directed at solving this anomaly.

There are a number of complications which make this a difficult system to investigate in further detail. Firstly, III, in the presence of excess RNC reacts to give salts $[\eta^5\text{-}C_5H_5Mo(RNC)_4]^+$ (benzene, reflux). In the event that the substitution of a reagent by RNC is a slow process compared to salt formation, quantitative data for the rate process becomes difficult to obtain. Secondly, III, on heating, is known to give rise to $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2$ (V) [25]. Whether the existence of small amounts of this triply bonded species plays an important role in the catalytic reaction we have been observing, is unknown. V is known to react with nucleophiles, L, to give $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4L_2$ and the substituted dimer (L = RNC) could be envisaged as readily forming reactive radicals (see experiment (6) above).

In conclusion, our results indicate that the role of catalysts in organometallic substitution reactions should give rise to a wide range of hitherto unknown compounds. Further, our finding that a non-chain mechanism is a viable pathway has implications for the study of catalytic systems involving organic reagents. Our present research programme is directed towards exploring this facet of the above reaction pathway.

Acknowledgement

I thank the CSIR and the University for financial support.

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