

A Synthetic Route to $M(\text{CO})_{6-n}(\text{RNC})_n$ ($M = \text{Cr}, \text{Mo}, \text{W}; n = 1-6$) from $M(\text{CO})_6$ and Isonitriles

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There is at present considerable interest in synthetic routes to the electron rich group 6 complexes $M(\text{CO})_{6-n}(\text{RNC})_n$ ($M = \text{Cr}, \text{Mo}, \text{W}; n = 1-6$, RNC = isonitrile) [1, 2]. This arises in part from their possible relevance in solar energy conversion [3]. Synthetic routes to these complexes ($n > 3$) are, however, limited and typically involve reductive cleavage of dinuclear metal-metal bonded species ($n = 6$) [1, 2] or reduction of metal(II) salts ($n = 6$) [3-5]. In only one instance has the synthesis of complexes with $n = 4-6$ been achieved directly from $M(\text{CO})_6$ ($M = \text{Cr}$) and this had involved ligand exchange between $M(\text{CO})_6$ and $M(\text{RNC})_6$ at high temperatures [6].

Recently, we reported that the complexes $M(\text{CO})_{6-n}(\text{RNC})_n$ ($n = 1-3$) could readily be prepared in high yield from $M(\text{CO})_6$ and isonitrile in the presence of CoCl_2 as catalyst [7]. In a continuation of this work we have now found that in the presence of PdO as catalyst, complete (and partial) CO substitution of $M(\text{CO})_6$ by RNC can also be achieved.

Addition of XyNC (2,6-dimethylphenylisocyanide) (1.1, 2.1 and 3.2 mmol) to $\text{W}(\text{CO})_6$ (1 mmol) and PdO (20 mg, Johnson-Matthey) as catalyst in

refluxing benzene (15 ml) rapidly (<5 min) leads to the complexes $\text{W}(\text{CO})_{6-n}(\text{XyNC})_n$ ($n = 1-3$) in high yield. The required complexes typically contain 10-15% of higher substituted derivatives which indicates the ease of the substitution reaction (*Note* $\text{W}(\text{CO})_5(\text{XyNC})$ can be prepared at room temperature *via* this route). In the absence of catalyst, difficulty is experienced in obtaining even the replacement of one CO group. The higher substituted derivatives are obtained more slowly by the addition of XyNC (1.1, 2.3, 4 mmol) to *fac*- $\text{W}(\text{CO})_3(\text{XyNC})_3$ (1 mmol) and PdO (20 mg) in refluxing toluene (10 ml) and yield *cis*- $\text{W}(\text{CO})_2(\text{XyNC})_4$ (0.5 h), $\text{W}(\text{CO})(\text{XyNC})_5$ (3 h) and $\text{W}(\text{XyNC})_6$ (24 h) respectively.

Similar results have also been obtained for the synthesis of $M(\text{CO})_{6-n}(\text{XyNC})_n$ ($M = \text{Mo}, \text{Cr}; n = 1-6$) with the exception of $\text{Cr}(\text{XyNC})_6$ which is only obtained in a yield of ~5% (36 h) as detected by n.m.r. spectroscopy. Since the catalysed reaction between PhNC and $\text{Cr}(\text{CO})_6$ does yield $\text{Cr}(\text{PhNC})_6$ in good yield (>50%, 24 h) our inability to prepare $\text{Cr}(\text{XyNC})_6$ must be due to steric crowding of the five XyNC groups in the $\text{Cr}(\text{CO})(\text{XyNC})_5$ molecule [3].

As expected, the reaction between $M(\text{CO})_6$ and alkyl isonitriles proceeds more slowly [8]. Thus, the reaction in refluxing toluene between $\text{Mo}(\text{CO})_6$ and Bu^tNC gives *cis*- $\text{Mo}(\text{CO})_2(\text{Bu}^t\text{NC})_4$ [9] (70%, 12 h) while the reaction between $\text{Mo}(\text{CO})_6$ and PhCH_2NC gives $\text{Mo}(\text{CO})(\text{PhCH}_2\text{NC})_5$ (60%, 10 h).

All the new complexes have been completely characterized by i.r. and n.m.r. spectroscopy and the data for the series $\text{W}(\text{CO})_{6-n}(\text{XyNC})_n$ ($n = 1-6$) are given in Table I. The number, intensity and peak positions of the data obtained from the i.r. and n.m.r. spectra are in agreement with the structures shown in Fig. 1. This series beautifully highlights the effect of replacing CO (a good π acceptor) with XyNC (a

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TABLE I. I.r. and N.m.r. Data for the New Tungsten-Isonitrile Complexes.

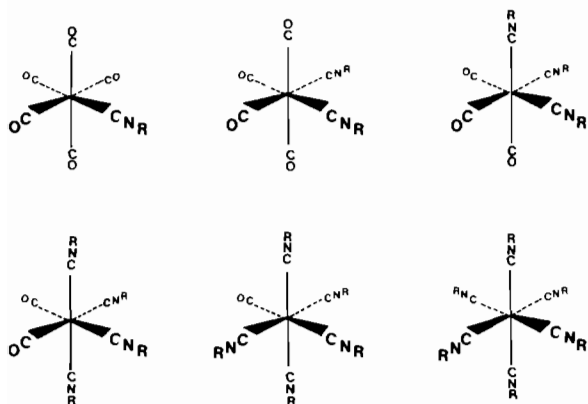
	i.r. (cm^{-1}) ^a		n.m.r. (δ/ppm) ^b
	$\nu(\text{NC})$	$\nu(\text{CO})$	
$\text{W}(\text{CO})_5(\text{XyNC})$	2135	2055 1950	1.89
<i>cis</i> - $\text{W}(\text{CO})_4(\text{XyNC})_2$	2138 2083	2003 1934 1924	2.06
<i>fac</i> - $\text{W}(\text{CO})_3(\text{XyNC})_3$	2135 2054	1938 1888	2.19
<i>cis</i> - $\text{W}(\text{CO})_2(\text{XyNC})_4$	2120 2015 1985	1893 1865	2.36, 2.31 ^c
$\text{W}(\text{CO})(\text{XyNC})_5$	2113 2013 1969	1861	2.43, 2.39 ^d
$\text{W}(\text{XyNC})_6$	2012 1951		2.48
$\text{W}(\text{CO})_3(\text{XyNC})_2\text{I}_2$	2155	2040 1986 1955	2.24
$\text{W}(\text{CO})_2(\text{XyNC})_3\text{I}_2$	2170 2145 2130	1984 1930	2.35
$\text{W}(\text{CO})(\text{XyNC})_4\text{I}_2$	2125 2105 2082	1916	2.46

^aRecorded in CHCl_3 , 2200-1600 cm^{-1} region

^bRecorded in C_6D_6 .

^cRatio 1:1.

^dRatio 4:1.



poorer π acceptor), the n.m.r. absorptions consistently show an upfield shift on substitution while the i.r. data consistently indicate a lowering of both $\nu(\text{CO})$ and $\nu(\text{NC})$ absorptions on substitution.

Although the *fac*-isomer of $\text{Cr}(\text{CO})_3(\text{XyNC})_3$ is obtained from our reaction mixtures, thermal isomerisation to *mer*- $\text{Cr}(\text{CO})_3(\text{XyNC})_3$ (~25%, 2 h) can be achieved [9], no evidence for catalysis of this isomerisation in the presence of PdO has, however, been detected

The facile, high yield synthesis of this series of electron rich metal(0) complexes provides a ready entry, *via* oxidation, into the synthesis of hepta-coordinate metal(II) complexes [1, 10–12]. In preliminary studies we have investigated the reactions between $\text{M}(\text{CO})_{6-n}(\text{RNC})_n$ ($n = 1-6$) and I_2 . For instance, addition of I_2 in CHCl_3 , to a solution of $\text{W}(\text{CO})_4(\text{XyNC})_2$ (or $\text{W}(\text{CO})_3(\text{XyNC})_3$) in CHCl_3 at room temperature, rapidly yields $\text{W}(\text{CO})_3(\text{XyNC})_2\text{I}_2$ (or $\text{W}(\text{CO})_2(\text{XyNC})_3\text{I}_2$). Since these W(II) complexes only react slowly with XyNC to yield $\text{W}(\text{CO})_2(\text{Xy-}$

$\text{NC})_3\text{I}_2$ and $\text{W}(\text{CO})(\text{XyNC})_4\text{I}_2$ respectively, the oxidation reaction involves initial replacement of CO, and not initial replacement of XyNC followed by the substitution of CO by free XyNC. The reactions between $\text{W}(\text{CO})_{6-n}(\text{XyNC})_n$ ($n = 4-6$) and I_2 yield a variety of products and these are presently under investigation.

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