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Nucleophilic Attack at Coordinated Carbon.
1. The Formation of Methoxyphenylcarbenetetracarbonyl (*p*-tolyl-isocyanide)tungsten(0)

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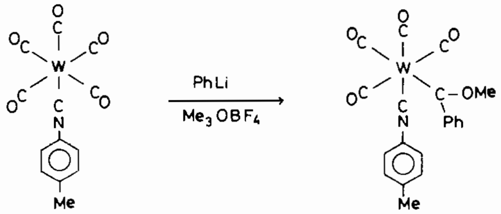
Introduction

Group VI metal hexacarbonyls undergo facile nucleophilic attack at the carbonyl carbon when exposed to strong bases such as phenyllithium. The resulting anion can then be alkylated to form a phenylalkoxycarbene complex [1]. Isocyanides coordinated to zero-valent transition metals are formally isoelectronic with CO at the metal center, suggesting the possibility that coordinated isocyanide might be susceptible to similar nucleophilic attack.

While higher-valent metal isocyanide complexes are attacked by relatively weak bases [2], low valent Group VI metal aryl isocyanide complexes surprisingly do not follow suit. For example, we found Cr-$(CNPh)_6$ to be inert towards attack by both phenyllithium and methyllithium in ether and refluxing benzene, with only starting materials recovered. Even with only one isocyanide ligand nucleophilic attack appears to occur preferentially at the carbonyl carbon. Addition of C_6H_5Li to $W(CO)_5(CN$*p*-tol) followed by methylation produced the title complex as the only observed product, with no direct evidence of attack at the isocyanide carbon:



Experimental

50 g of *1* (1.14 mmol) in 25 ml of dry deoxygenated ether in a 3 neck flask equipped with magnetic stir bar, nitrogen adaptor and addition funnel received 1.14 mmol C_6H_5Li in 10 ml ether over a period of 20 minutes. The resulting yellow-brown solution was stirred an additional hour then evaporated to dryness by a stream of N_2. 20 ml of pentane was added to the brown residue followed by approximately 1.1 mmol $[(CH_3)_3O]BF_4$ in 5 ml deoxygenated water. After vigorous stirring the pentane layer turned dark red. The layers were separated and the pentane solution was dried over $MgSO_4$. The unreacted starting material was separated from the product by precipitation of the starting material at –45°. The purified product was recrystallized from pentane at –60°. The isocyanide pentacarbonyl complex appears to be less reactive towards nucleophilic attack than the hexacarbonyl complex in that varying amounts of starting material were recovered after adding equimolar amounts of C_6H_5Li, even with extended reaction time.

The crystalline dark red complex is reasonably air-stable in the solid state and is soluble in most organic solvents. The structural assignment is based on ^{13}C NMR and IR data. ^{13}C NMR (TMS): Carbene carbon-231 ppm, methyl (carbene)-69.4 ppm, methyl(*p*-tolyl)-21.3 ppm, aromatic resonances–*ca.* 126–134 ppm, carbonyl carbons–208.8 ppm, 202.6 ppm, 200.2 ppm. The carbonyl resonances are in a 1:1:2 integral ratio, consistent with *cis* geometry for the two non-carbonyl ligands. IR (hexane solution) ν_{CN}: 2104 cm^{-1}; ν_{CO}: 2005 cm^{-1}, 1955 cm^{-1}, 1940 cm^{-1}, 1920 cm^{-1}. The same reaction with $Mo(CO)_5(CN$–*p*-tol) also produced a dark red complex, and preliminary data indicate that it reacts in the same fashion as the tungsten analogue. However, the molybdenum complex is much less stable than the tungsten complex and we were unable to characterize it unequivocally. It is interesting to note that this difference in stability between molybdenum and tungsten complexes also occurs with $CO_5W(C(OMe)Ph)$ and $CO_5Mo(C(OMe)Ph)$ [3]. This work is in agreement with studies by J. A. Connor, *et al.*, which indicated that an alkylisocyanide pentacarbonylchromium complex (R = t-butyl) underwent nucleophilic attack, but the isocyanide was left intact [4, 5].

Discussion

The C–N stretching frequency for $(CO)_4W(CN$*p*-tol)(C(OMe)Ph) occurs 36 cm^{-1} lower than for $(CO)_5W(CN$*p*-tol), suggesting increased $d\pi$–$p\pi^*$ back donation onto the isonitrile carbon when a carbonyl ligand is formally replaced with a carbene ligand. This is not surprising in that earlier work strongly suggests that carbenes do not compete effectively with carbon

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monoxide for π metal electron density [6], while aryl isocyanides have been reported to be even better π-acceptors than CO [7, 8]. The increased π-acceptor ability of ArCN might in part explain why aryl isocyanides appear to be less electrophilic than coordinated carbon monoxide.

$(CO)_4W(CNp\text{-tol})(C(OMe)Ph)$ contains three major types of metal-carbon bonds attached to the same metal center: M–C=, M–CO, M–CNR; and is currently undergoing crystallographic investigation. Further work utilizing alkyl isocyanides in place of aryl isocyanides is also underway.

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