Synthesis of transition metal isocyanide compounds from carbonyl complexes *via* reaction with Li[Me₃SiNR][†][‡]

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The reaction between a transition metal carbonyl compound, L_nMCO , and Li[Me₃SiNR] yields the corresponding isocyanide derivative, L_nMCNR , thereby providing a new route to transition metal isocyanide compounds that does not require the use of free isocyanides as reagents.

Isocyanides (RNC) feature prominently in transition metal chemistry by virtue of their ability to serve as combined σ -donor and π -acceptor ligands.¹⁻³ While this dual feature of the bonding is common to CO, an important distinction between RNC and CO is that the steric and electronic properties of isocyanides may be effectively tuned by modifying the substituent on nitrogen. Indeed, this aspect has been of benefit in the application of transition metal isocyanide complexes as catalysts for organic transformations.⁴⁻⁷ Despite their widespread use, however, the majority of transition metal isocyanide complexes feature rather simple substituents on nitrogen, a reflection of the paucity of readily available commercial isocyanide compounds. Progress in transition metal isocyanide chemistry would, therefore, be facilitated by the development of new synthetic methods that do not require the use of the isocyanide as a reagent. Two such approaches include (i) the formal addition of R^+ to the nitrogen atom of a metal cyanide ligand^{1b,c,f} and (ii) the formal replacement of the oxygen atom of a metal carbonyl ligand by an NR group.⁸⁻¹⁰ The latter is a particularly appealing approach in view of the ubiquity of transition metal carbonyl compounds, and here we describe a new method that utilizes Li[Me₃SiNR] as a reagent for converting a carbonyl compound into its isocyanide counterpart.

The carbon atom within a metal carbonyl moiety, L_nMCO , is well known to be susceptible to nucleophilic attack by external reagents.¹¹ For example, attack by carbon nucleophiles has been employed in the syntheses of Fischer carbene complexes,¹² while attack by oxygen nucleophiles features prominently in the mechanisms of (i) the water-gas shift reaction,¹³ (ii) the exchange of oxygen atoms between a carbonyl ligand and H₂O,¹⁴ and (iii) the Me₃NO induced dissociation of a carbonyl ligand as CO₂.¹⁵ The carbon atom of L_nMCO is also susceptible to attack by nitrogen based nucleophiles^{16,17} which provides, in principle, a first step for converting a carbonyl to an isocyanide ligand. In this regard, we report that the conversion of L_nMCO to L_nMCNR may be achieved *via* treatment of the metal carbonyl with Li[Me₃SiNR], a reagent that may be generated by, for example, treatment of RNH₂ with Me₃SiCl followed by BuⁿLi.¹⁸ Furthermore, since primary amines are commonly used precursors for free isocyanides,^{1/,19} it is evident that this method enables the synthesis of metal isocyanide compounds from RNH₂ without having to synthesize first the free isocyanide. In addition to the synthetic simplicity, this method has the advantage of eliminating problems associated with the putrid smell of the free isocyanide compounds.¹⁹⁶

For example, $M(CO)_6$ reacts with $Li[Me_3SiNBu^t]^{20}$ to yield mono, bis, tris and tetrakis derivatives, namely $M(CO)_5(CNBu^t)$ (M = Cr, Mo, W), $cis-M(CO)_4(CNBu^t)_2$ (M = Cr, Mo, W), $fac-M(CO)_3(CNBu^t)_3$ (M = Cr, Mo, W), and $cis-M(CO)_2$ - $(CNBu^t)_4$ (M = Mo), as illustrated in Scheme 1. The syntheses of the molybdenum compounds $Mo(CO)_{6-n}(CNBu^t)_n^{21}$ is of note in view of their recent use as catalysts for organic transformations.⁵ While the isocyanide complexes $M(CO)_{6-n}(CNBu^t)_n$ have been previously synthesized by reactions employing Bu^tNC as a reagent,²² we have determined the molecular structures of $Cr(CO)_5(CNBu^t)$, $cis-M(CO)_4(CNBu^t)_2$ (M = Cr, Mo, W), $fac-W(CO)_3(CNBu^t)_3$,²³ and $cis-Mo(CO)_2(CNBu^t)_4$ by X-ray diffraction.

The synthetic method is not restricted to the Group 6 metals, as illustrated by the fact that Li[Me₃SiNBu¹] also reacts with Fe(CO)₅ to give *axial*-Fe(CO)₄(CNBu^t) and *trans*-Fe(CO)₃(CNBu¹)₂ (Scheme 1). While a variety of compounds of the class Fe(CO)_{5-n}(CNR)_n are known,²⁴ the only structurally characterized heteroleptic examples of which we are aware are disubstituted derivatives Fe(CO)₃(CNR)₂, namely Fe(CO)₃(CNMe)₂²⁵ and Fe(CO)₃(CNBu^t)₂.²⁶ The molecular structure of monosubstituted Fe(CO)₄(CNBu^t) is, therefore, presented in Fig. 1, thereby demonstrating that the isocyanide ligand adopts an axial position, with an Fe–C bond length (1.89 Å) that is distinctly longer than those of the carbonyl ligands (1.79–1.81 Å).

In addition to the synthesis of Bu^tNC complexes, the method may also be employed to obtain complexes that feature other isocyanide ligands. For example, the arylisocyanide derivatives Mo(CO)₅(CNAr) (Ar = p-C₆H₄Me,²⁷ p-C₆H₄OMe³) and Mo(CO)₄(CNAr)₂ (Ar = 2,4,6-C₆H₂Me₃) have been synthesized by this approach, of which Mo(CO)₅(CN-p-C₆H₄OMe) and Mo(CO)₄(CN-2,4,6-C₆H₂Me₃)₂ have been structurally characterized by X-ray diffraction.

Since attention has recently been given to the application of isocyanide ligands that feature $bulky^{6,28,29}$ and chiral⁸ substituents, we have evaluated the ability to synthesize such complexes *via* Li[Me₃SiNR]. For example, the adamantyl

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Fig. 1 Molecular structure of *axial*-Fe(CO)₄(CNBu^t).

complexes Mo(CO)₅(CN-1-Ad) and *cis*-Mo(CO)₄(CN-1-Ad)₂ may be synthesized by this approach (Scheme 1) and have been structurally characterized by X-ray diffraction (see, for example, Fig. 2).³⁰ Likewise, the enantiomerically pure (R)-1,2,3,4-tetrahydro-1-naphthyl derivative, Mo(CO)₅(CN-1-Np^{H4}), has also been isolated and structurally characterized (Fig. 3). Compared to tertiary phosphine counterparts, enantiomerically pure isocyanide ligands have been little employed in transition metal chemistry,⁸ and the synthetic transformation described here provides a simple means to access transition metal compounds of such ligands from the chiral amine.

The mechanism proposed for the conversion of the carbonyl ligand to an isocyanide ligand is illustrated in Scheme 2, with the essential features involving nucleophilic attack by $[Me_3SiNR]^-$ on the carbonyl carbon of L_nMCO to generate a silylcarbamoyl intermediate $L_nM[C(O)N(R)SiMe_3]^-$, followed by elimination of $Me_3SiO^{-.31-34}$ Precedent for this mechanism is provided by the fact that lithium amides are



Fig. 2 Molecular structure of Mo(CO)₅(CN-1-Ad).



Fig. 3 Molecular structure of $Mo(CO)_5(CN-1-Np^{H_4})$.

known to react with CO to generate $[R_2NC(O)Li]^{35}$ and that silyl derivatives of the type $[(R_3Si)N(R)C(O)Li]$ decompose to give RNC and $R_3SiOLi.^{34}$

The overall carbonyl-isocyanide conversion employing RNH₂ is related to the observation that thiocarbonyl compounds react with RNH2 to generate the isocyanide derivative, accompanied by elimination of H₂S.³⁶ An important distinction between the reactivity of carbonyl and thiocarbonyl ligands, however, is that the required elimination of H₂O to convert a carbonyl to an isocyanide derivative is not a facile process. Thus, carbonyl compounds simply react with RNH₂ (but not aryl amines) to give carbamoyl derivatives of the type $\{L_n M[C(O)NHR]\}[RNH_3]^{16}$ and conversion to L_nMCNR requires treatment with dehydrating agents such as C(O)Cl₂ and [C(O)Cl]₂.¹⁰ For example, CpFe(CO)₂-[C(O)NHMe] reacts with $C(O)Cl_2$ in the presence of Et₃N to give [CpFe(CNMe)]Cl.^{10a} The ability of Li[Me₃SiNR] to achieve deoxygenation of the carbonyl ligand may be attributed to the strength of the Si-O bond which provides a driving



force for the reaction. In this regard, the use of Li[Me₃SiNR] to effect the CO–CNR conversion of a carbonyl compound is analogous to the formation of isocyanide compounds by using phosphorimidates, Li[(EtO)₂(O)PNR],⁸ and phosphinimines, R_3PNR' ,⁹ for which P–O bond formation presumably provides the driving force.

While the formation of an isocyanide complex by reaction of a thiocarbonyl derivative with RNH₂ may be considered a more appealing direct method of synthesis than is the reaction of a carbonyl complex with Li[Me₃SiNR], a downside of the former route is that compounds which feature thiocarbonyl ligands are much less common than carbonyl derivatives.³⁷ Therefore, the reaction of a carbonyl derivative with Li[Me₃SiNR] provides a convenient alternative for the synthesis of isocyanide compounds from carbonyl derivatives. In addition, another advantage of using Li[Me₃SiNR] to synthesize transition metal isocyanide compounds is that Li[Me₃SiNR] derivatives are obtained from primary amines, which are more readily available commercially than are isocyanides.

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