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ESR Studies of the Reaction of Group 11 Metal Atoms with Alkyl Cyanides and Isocyanides in a Rotating Cryostat[†,1]

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Group 11 metal atoms have been deposited into inert hydrocarbon matrices with a variety of organic cyanides in a rotating cryostat at 77 K, and the electron spin resonance spectra of the deposits have been examined. The spectra demonstrate that metal atoms react with organic cyanides to give monoligand π-complexes M[RCN] with either side-on or end-on bonding between the ligand and the metal atom. Addition to the nitrile function also occurs to give organometallic iminyls $RC(M){=}\dot{N}$. There is evidence for cis and trans stereoisomeric forms of this radical although a bridged structure and an organometallic imidoyl cannot be completely eliminated.

Introduction

We have recently reported ESR spectra[3,4] obtained from reaction of the group 11 metal atoms Cu, Ag, and Au (M) with hydrogen cyanide at 77 K in a rotating cryostat. The principal paramagnetic products of these reactions, deduced from the spectra, are the organometallic iminyls $MCH{=}\dot{N}$[4] for all three metals and the monoligand complexes of M[HCN][4] for Cu and Ag but not Au. There was tentative evidence that β-copper and β-silver iminyls can exist as cis and trans stereoisomers, but there was no evidence for the formation of the isomeric imidoyls $MN{=}\dot{C}H$. In the case of Cu only one M[HCN] complex was formed with side-on bonding between the ligand and the metal atom but Ag gave two complexes, a side-on bonded species and one with end-on bonding between the nitrogen and the metal atom.

In the hope of determining the generality of these observations, we have investigated the paramagnetic products of the reaction of group 11 metal atoms with alkyl cyanides in a rotating cryostat. In addition these metal atoms have been allowed to react with isocyanides in an attempt to prepare authentic organometallic imidoyls. The results of this work are reported in this article.

Experimental Section

The rotating cryostat, electron spin resonance spectrometer, method used to vaporize group 11 metal atoms, calibration of ESR spectra, and method used to calculate ESR parameters have been described previously.[5] All spectra were first recorded at 77 K and then annealed with the aid of a variable-temperature accessory. Unpaired s spin populations were estimated relative to the one-electron parameters calculated by Morton and Preston.[6]

Adamantane and cyclohexane were used as inert matrices. Pivalonitrile, acetonitrile, benzonitrile, perdeuterioacetonitrile, and acrylonitrile were obtained from commercial sources and used as received. The isocyanides were prepared by standard procedures.

Results

Alkyl Cyanides. $(CH_3)_3CCN$. Reaction of ^{63}Cu atoms with $(CH_3)_3CCN$ in adamantane at 77 K gives an ESR spectrum (Figure 1) which consists of transitions from at least five species. The weak line at ~5600 G, labeled A, is the $M_I = -^3/_2$ ESR transition from isolated ^{63}Cu atoms.[7] The spectrum labeled B has broad lines ($\Delta H_{pp} \approx 100$ G) and the ESR parameters $a_{63} = 1283$ G and $g = 2.0057$. The copper hyperfine interaction (hfi) is similar to the values for the copper monoligand complexes $Cu[C_2H_2]$,[8] $Cu[C_2H_4]$,[8] $Cu[C_6H_6]$,[5] and Cu[HCN].[4] We, therefore, assign the spectrum to the monoligand complex $Cu[(CH_3)_3CCN]$. The lines are, however, much wider than those from Cu[HCN]. The dominant feature in the center of the spectrum consists of *two* quartets, the low- and high-field lines of which are labeled C and D in Figure 1, with broad lines and a marked M_I effect on the intensity of the transitions. The parameters for these species are as follows: species C, $a_{63} = 419.5$ G (1174 MHz), $g = 2.0022$, and species D, $a_{63} = 339.4$ G (949 MHz), $g = 1.9984$. Transitions C and D are not the parallel and perpendicular features of the anisotropic spectrum of a single species because C is less stable than D upon annealing and does not return upon recooling. These species have Cu hfi similar to the values for Cu adducts to HCN and are almost certainly adducts of Cu to $(CH_3)_3CCN$. In addition to these radicals there is a narrow isotropic ten-line spectrum, E, which is readily assigned to *tert*-butyl with $a_H(9) = 23$ G. Annealing experiments apart from distinguishing between C and D demonstrate that Cu atoms, $Cu[(CH_3)_3CCN]$, C and D decay rapidly and that $(CH_3)_3\dot{C}$ grows in intensity.

The complex ESR spectrum produced by reaction of ^{107}Ag atoms with $(CH_3)_3CCN$ is shown in Figure 2. The outer lines, labeled A, are from isolated Ag atoms in two nonequivalent trapping sites ($a_{107} = -611$ G, $g = 2.0011$, and $a_{107} = -598$ G, $g = 2.0016$). The spectrum labeled B consists of a doublet of triplets indicating that the species responsible for this spectrum contains one Ag and one nitrogen atom. It has the following parameters: $a_{107} =$

[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

(1) (a) Issued as NRCC No. 24180. (b) For the previous papers in this series see: Howard, J. A.; Sutcliffe, R.; Mile, B. *J. Catal.* **1984**, *90*, 156–159; *Chem. Phys. Lett.* **1984**, *112*, 84–86.

(2) NRCC Research Associate.

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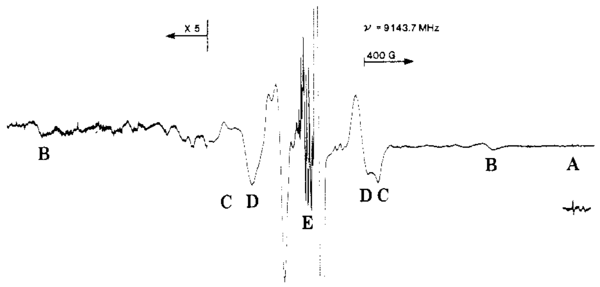

Figure 1. ESR spectrum obtained from adamantane containing ^{63}Cu and $(CH_3)_3CCN$.

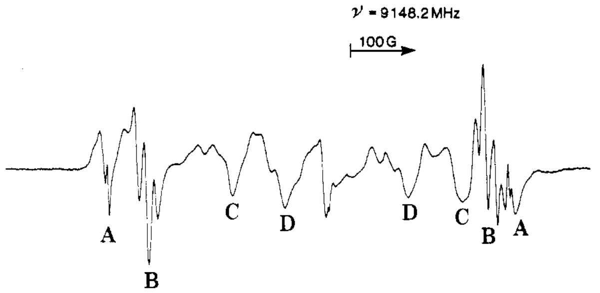

Figure 2. ESR spectrum obtained from adamantane containing ^{107}Ag and $(CH_3)_3CCN$.

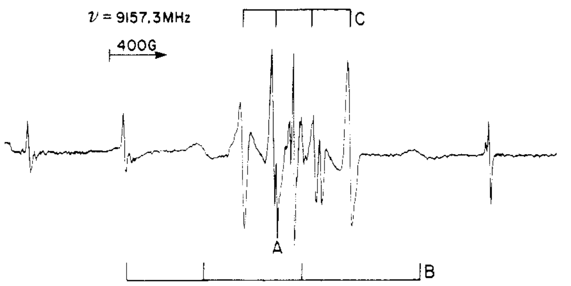

Figure 3. ESR spectrum obtained from adamantane containing Au and $(CH_3)_3CCN$.

−508 G, A_N = 14 G, and g = 1.9988 which are close to those for the side-on-bonded π-complex Ag[HCN].[3] This species is, therefore, almost certainly the monoligand complex Ag[$(CH_3)_3CCN$] with side-on bonding between the ligand and metal atom. The broad lines labeled C and D have the following parameters: a_{107} = −346.8 G and g = 1.995 and a_{107} = −186.3 G and g = 1.999. Both spectra have poorly resolved triplet interactions from one nitrogen nucleus with $A_N \approx 20.4$ G. Clearly both C and D contain one Ag and one N atom. D has parameters very similar to the radical that has been identified as *trans*-HC(Ag)=$\dot{N}$[3] and also the iminyl $CH_3C(Ag)=\dot{N}$[9] formed by γ-irradiation of $AgClO_4$ in CH_3CN at 77 K. We, therefore, feel fairly confident in suggesting that D is the organosilver iminyl $(CH_3)_3CC(Ag)=\dot{N}$. C has a Ag hfi which appears too large for an iminyl.[3] It is, therefore, probably a π-complex with end-on bonding between the ligand and metal atom.

Reaction of Au atoms with $(CH_3)_3CCN$ gives the spectrum shown in Figure 3. Apart from Au atoms in one major trapping site, labeled A, with a_{Au} = 1043.5 G and g = 2.0019, there are two quartets labeled B and C in Figure 3. The quartet B has broad lines and a_{Au} = 675 G and g = 2.028, parameters which were calculated from the $M_I = -^3/_2$ and $^1/_2$ transitions. The $M_I = -^1/_2$ and $^3/_2$ lines in the stick diagram were predicted from this analysis. This species has a Au hfi consistent with it being the monoligand complex Au[$(CH_3)_3CCN$]. Treating the lines labeled C as isotropic gives a_{Au} = 248.2 G and g = 1.9923. These parameters are similar to those for the organogold iminyl AuC(H)=$\dot{N}$,[3] and we assign them to the related radical $(CH_3)_3CC(Au)=\dot{N}$. Annealing experiments reveal that Au[$(CH_3)_3CCN$] decays rapidly at 100 K, $(CH_3)_3CC(Au)=\dot{N}$ decays slowly at 173 K, and $(CH_3)_3\dot{C}$ is formed at a rate which is close to the rate of disappearance of the iminyl.

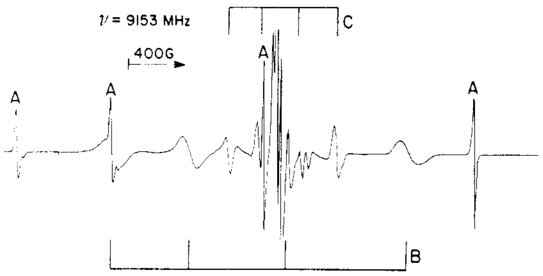

Figure 4. ESR spectrum obtained from adamantane containing Au and CD_3CN.

CH_3CN. ^{63}Cu atoms and CH_3CN give two essentially isotropic quartets with a_{63} = 350 G and g = 2.0044 and a_{63} = 293 G and g = 2.0025. Both spectra show a marked M_I effect on line intensities with the $M_I = -^1/_2$ transition very much more intense than the other three transitions. When the sample is warmed above 77 K, the species with the larger Cu hfi decays first but no methyl is detected. The magnitude of the Cu hfi for these two species suggest that they are adducts of Cu to CH_3CN. At 77 K the central region of the spectrum is dominated by the spectrum from $NC\dot{C}H_2$ (a_H (2) = 21 G and g = 2.002) which may have been produced by H atom abstraction from CH_3CN by Cu atoms or microcrystallites. These parameters are in good accord with those reported by Egland and Symons[10] for this radical prepared by γ-irradiation of solid CH_3CN.

CD_3CN gives similar spectrum to CH_3CN, but there is none of the line sharpening which is usually found when protonated substrates are replaced by their deuterated analogues.

^{107}Ag atoms and CD_3CN in adamantane give a spectrum that is identical, except for poorer resolution, to the spectrum for Ag and $(CH_3)_3CCN$ shown in Figure 2. Thus three species, apart from ^{107}Ag atoms, can be identified; the side-on bonded complex Ag[CD_3CN] (a_{107} = −508 G, A_N = 14 G, and g = 1.999), the end-on bonded complex Ag[CD_3CN] (a_{107} = −346.8 G, $A_N \approx 20.4$ G, and g = 1.995), and an organosilver iminyl (a_{107} = −186 G, A_N = 20.4 G, and g = 1.999).

Au and CD_3CN in adamantane give the ESR spectrum shown in Figure 4. The quartet labeled A is from Au atoms in one dominant trapping site. The broad quartet (ΔH_{pp} = 100–130 G) labeled B has the parameters a_{Au} = 684.5 G and g = 2.0275 and is assigned to the monoligand complex Au[CD_3CN]. In addition to these two quartets there is a quartet labeled C in the central region with a_{Au} = 253 G and g = 2.000 G. The spectrum from this species shows a marked quadrupole effect on the line positions, and the $M_I = -^1/_2$ line is split into two, and there is evidence for deuterium and nitrogen hyperfine interactions. This spectrum is assigned to the organogold iminyl $CD_3C(Au)=\dot{N}$. The central region of the spectrum is dominated by a broad anisotropic line from Au aggregates and microcrystallites.

Annealing experiments reveal that Au[CD_3CN] is extremely unstable and disappears at 100 K, in fact before

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[9] Symons, M. C. R.; Alesbury, C. K. *J. Organomet. Chem.* **1978**, *162*, C27–C30.

[10] Egland, R. J., Symons, M. C. R. *J. Chem. Soc. A* **1970**, 1326–1329.

Table I. ESR Parameters for Group 11 Complexes with Alkyl Cyanides[a]

complex	species	a_M/G[b]	ρ_M	A_N/G	g factor
$Cu[(CH_3)_3CCN]$	B	1283 (3601.6)	0.63	c	2.0057
$Ag[(CH_3)_3CCN]$	B	−508 (−1422)	0.78	14	1.9988
$Ag[(CH_3)_3CCN]$	C	−346.8	0.53	20.4	1.995
$Au[(CH_3)_3CCN]$		675 (944.7)	0.66	c	2.028
$Ag[CD_3CN]$		−508 (−1422)	0.78	14	1.999
$Ag[CD_3CN]$		−346.8	0.53	20.4	1.995
$Au[CD_3CN]$		684.5	0.67	c	2.0275
$Cu[C_6H_5CN]$		~1300	0.63	c	
$Ag[C_6H_5CN]$		−554.8 (−1554.9)	0.85	c	2.0024
Cu[HCN]		1386-1505	0.68	c	2.01-2.02
Ag[HCN][d]		−570.6	0.87	9.6	2.001
Ag[HCN][e]		−462.7	0.71	21.3	1.9994

[a] In adamantane at 77 K. [b] Values in parentheses are in MHz. [c] Not resolved. [d] Side-on bonded complex. [e] End-on bonded complex.

Table II. ESR Parameters for Group 1B Adducts to Alkyl Cyanides[a]

adduct	species	a_M/G	ρ_M	A_N/G	g factor
$(CH_3)_3CC(Cu){=}\dot{N}$	C	419.5	0.2	b	2.0022
$(CH_3)_3CC(Cu){=}\dot{N}$	D	339.4	0.16	b	1.9984
$(CH_3)_3CC(Ag){=}\dot{N}$	D	−186.3	0.28	20.4	1.999
$(CH_3)_3CC(Au){=}\dot{N}$		248.2	0.24	b	1.9923
$CH_3C(Cu){=}\dot{N}$		350.2	0.16	b	2.0044
$CH_3C(Cu){=}\dot{N}$		293.2	0.14	b	2.0025
$CD_3C(Ag){=}\dot{N}$		−186	0.28	≃20.4	1.999
$CD_3C(Au){=}\dot{N}$		253	0.25	b	2.000
$C_6H_5C(Ag){=}\dot{N}$		−100	0.15	≃23	
$C_6H_5C(Au){=}\dot{N}$		~250	0.24	b	
CH_2CHCN/Cu		134.2	0.06	b	2.005
CH_2CHCN/Ag		−136.6	0.21	b	2.001
CH_2CHCN/Au		217.7	0.21	b	1.9982
$HC(Cu){=}\dot{N}$[c]	A	479	0.22	b	2.001
	B	280	0.13	b	2.001
	C	372	0.17	b	1.998
$HC(Ag){=}\dot{N}$[c]	D	−185	0.31	b	2.0011
	E	−100	0.15	b	
$HC(Au){=}\dot{N}$[c]		268.5	0.26	b	1.997

[a] In adamantane at 77 K. [b] Not resolved. [c] Reference 3.

Au atoms. Most of the iminyl has decayed at 153 K, and the spectrum consists mainly of the broad anisotropic feature at the center.

C_6H_5CN. It has been reported previously[5] that Cu and C_6H_5CN give only clusters and microcrystallites and that there is no evidence for formation of $Cu[C_6H_5CN]$ or $C_6H_5C(Cu){=}\dot{N}$. More recent experiments have, however, shown evidence for a weak spectrum from $Cu[C_6H_5CN]$ with $a_{63} \approx 1300$ G and a poorly resolved central feature which could possibly be from $C_6H_5\dot{C}{=}NCu$. Ag, on the other hand, gives $Ag[C_6H_5CN]$ ($a_{107} = -554.8$ G and $g = 2.0024$) and an adduct with $a_{107} = -100$ G, $A_N \approx 23$ G, and $g = 2.000$ which was tentatively identified as $C_6H_5C(Ag){=}\dot{N}$. Similarly Au and C_6H_5CN give a species with a Au hfi of ~250 G which was identified as the adduct $C_6H_5C(Au){=}\dot{N}$.

$CH_2{=}CHCN$. Cu atoms and acrylonitrile give a spectrum consisting of a broad quartet with $a_{63} = 134.2$ G, $g = 2.005$, and four almost isotropic lines in the center of the spectrum. This latter spectrum is best analyzed in terms of a doublet of doublets from two nonequivalent hydrogen atoms with $a_H(1) = 74.5$ G, $a_H(1) = 33$ G, and $g = 2.000$. These parameters are close to the β-hydrogen coupling constants for vinyl[11] ($a_H(1) = 68$ G, $a_H = 34.2$ G), and we tentatively assign them to $CH_2{=}\dot{C}CN$ produced by abstraction of the α-proton from $CH_2{=}CHCN$ by a Cu atom or nascent copper cluster. This abstraction is similar to that found for CH_3CN and Cu atoms. Interestingly it is enhanced in neat acrylonitrile.

Ag atoms and $CH_2{=}CHCN$ give a spectrum consisting of one doublet with $a_{107} = -136.6$ G and $g = 2.001$ which can be assigned to an adduct radical. Au and CH_2CHCN also give one adduct radical with $a_{Au} = 217.7$ G and $g = 1.9982$. Neither Ag nor Au give any evidence for spectra which can be assigned to mono- or diligand π-complexes.

Alkyl Isocyanides. There is no evidence for isolated metal atoms or monoligand complexes when Cu, Ag, and Au are allowed to react with CH_3NC, $(CH_3)_3CNC$, and C_6H_5NC in adamantane at 77 K. The only paramagnetic species that are detected with CH_3NC and $(CH_3)_3CNC$ are CH_2NC ($a_H(2) = 21.17$ G, $a_N(1) = 6.84$ G, and $g = 2.0022$) and $(CH_3)_3C\cdot$ while the spectrum from C_6H_5NC is broad and anisotropic and has no features which can be attributed to C_6H_5NCM. If metal atoms react with this isocyanide to give C_6H_5, this radical would be expected to abstract a H atom from the matrix to give adamantyl.[12] Clearly the isocyanide function is extremely labile toward group 11 metal atoms, and the organometallic imidoyls are unstable at 77 K and undergo β-scission.

$$M + RNC \rightarrow [RN{=}\dot{C}M] \rightarrow R\cdot + N{\equiv}CM$$

Discussion

The ESR parameters and unpaired metal s spin populations (ρ_M) for the readily identified paramagnetic products from reaction of group 11 metal atoms with alkyl cyanides in a rotating cryostat at 77 K are gathered in Tables I and II. Included in these tables are the param-

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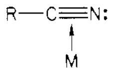
(12) Bennett, J. E.; Mile, B.; Thomas, A. *Proc. R. Soc. London, Ser. A* **1966**, *293*, 246–258.

eters that we have previously reported for HCN[3,4] and C_6H_5CN[5].

(i) Complexes. All three metal atoms react with $(CH_3)_3CCN$ to give monoligand π-complexes M[RCN] with 50–80% unpaired s spin population on the metal atom whereas monoligand complexes are only observed for CD_3CN with Ag and Au and for C_6H_5CN with Cu and Ag and not at all for $CH_2{=}CHCN$.

These complexes may have either side-on bonding (structure I) or end-on bonding (structure II) between the metal atom and the ligand as observed for Ag and HCN.[4]



$$\underset{\substack{\uparrow \\ M}}{R—C}\equiv N\!:$$

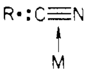
I

$$R—C\equiv N\!: \leftarrow M$$

II

The Cu hyperfine interaction (hfi) for $Cu[(CH_3)_3CCN]$ is only slightly less than the value for Cu[HCN] which, it has been concluded,[4] has side-on bonding. We are, therefore, tempted to conclude that $Cu[(CH_3)_3CCN]$ also has side-on bonding with slightly less unpaired s spin population on the metal atom than in Cu[HCN]. Cu does not appear to give an isolable end-on bonded complex with alkyl cyanides.

Like HCN, $(CH_3)_3CCN$ and CH_3CN give two complexes with Ag atoms, a side-on and end-on bonded complex, with ~78% and ~53% unpaired s spin population on the metal atom, respectively. These values are somewhat lower than the values of ρ_M for the two complexes given by HCN. This could be due to increased contributions from the excited structures III and IV or to a larger metal p contribution to the singly occupied molecular orbital because of the increased basicity of the π or lone-pair electrons in the alkyl cyanides. Quite significant p orbital participation in the SOMO would not be detected in our spectra. $Ag[C_6H_5CN]$ has ρ_M close to the value for side-on bonded Ag[HCN] which is consistent with a reduced involvement of structure III for $Ag[C_6H_5CN]$. $Au[(CH_3)_3CCN]$ and $Cu[(CH_3)_3CCN]$ have similar values of ρ_M suggesting side-on bonding for the Au complex.



$$R\cdot\!:\underset{\substack{\uparrow \\ M}}{C}\equiv N$$

III

$$R\cdot\!:C\equiv NM$$

IV

Nitrogen hfi are only resolved in the silver–alkyl cyanide complexes and are ~14 and ~20 G for the side-on and end-on bonded complexes, respectively. These values are similar to the values for the two Ag[HCN] complexes considering the poor resolution of our powder spectra. The line widths of the Cu and Au monoalkyl cyanide complexes suggest significant N hfi.

Comparison of ρ_M for M[RCN] with values of ρ_M for other group 11 monoligand π-complexes such as acetylenes,[8,13,14] arenes,[5] and olefins[8,14,15] indicates that the nature of the ligand has very little influence on the unpaired s spin population on the metal atom.

If the absence or presence of a complex gives some indication of the stability, then the end-on bonded complexes, only observed with Ag and alkyl cyanides, are less stable than the side-on bonded complexes. Similarly the stability of the side-on-bonded complexes depends on the nature of the metal atom and ligand. These differences must be associated with d–π^* overlap, i.e., back donation from the metal d orbitals to the ligand antibonding orbitals, which is greater for side-on than end-on bonded complexes.

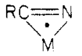
(ii) Adduct Radicals. Group 11 metal atoms react with alkyl cyanides to give species with 15-30% unpaired s spin population on the metal atom which are assumed to be adducts. There are three possible structures for adducts to alkyl cyanides; the organometallic iminyl V, the organometallic imidoyl VI, and the bridged radical VII.

$$RC(M){=}\dot{N}$$

V

$$R\dot{C}{=}NM$$

VI



VII

Of the adducts observed in this work the Au adducts are the most straightforward. Thus the Au hfi for adducts to $(CH_3)_3CCN$, CH_3CN, and C_6H_5CN are very similar to those for the imminyl $HC(Au){=}\dot{N}$ produced by addition of Au atoms to HCN.[3] We can, therefore, conclude that the alkyl cyanides give the iminyls $(CH_3)_3CC(Au){=}\dot{N}$, $CH_3C(Au){=}\dot{N}$, and $C_6H_5C(Au){=}\dot{N}$. Acrylonitrile and Au give an adduct with a somewhat smaller Au hfi. In this case, addition could also occur at the vinyl function to give the substituted alkyl $AuCH_2\dot{C}HCN$. The magnitude of the Au hfi does, however, suggest that it is an organogold iminyl in which the excited structure $CH_2{=}CH\dot{C}(Au){\equiv}N$ plays a less important role in the overall structure.

Ag atoms and $(CH_3)_3CCN$ and CH_3CN give one adduct with ρ_M and N hfi similar to the values that have been assigned to *trans*-$HC(Ag){=}\dot{N}$[3] in which the unpaired electron is located in a sp-hybridized orbital on nitrogen and the Ag atom is situated trans to this orbital. It should, however, be noted that these parameters for $RC(Ag){=}\dot{N}$ are similar to those that have been assigned to $CH_3C(Ag){=}\dot{N}$ with the unpaired electron in the p_z orbital on nitrogen.[9] The N hfi is then a parallel feature of an anisotropic interaction. C_6H_5CN and $CH_2{=}CHCN$ also give adducts with Ag atoms with ρ_M = 0.15 and 0.18, respectively. These values are similar to the values for *cis*-$HC(Ag){=}\dot{N}$, and it would be tempting to conclude that we have produced *cis*-$C_6H_5C(Ag){=}\dot{N}$ and *cis*-$CH_2{=}CHC(Ag){=}\dot{N}$. We cannot, however, exclude the possibility that addition has occurred at nitrogen to give the imidoyls $C_6H_5\dot{C}{=}NAg$ and $CH_2{=}CH\dot{C}{=}NAg$ with the unpaired electron located in a p_z orbital on the carbon atom. The N hfi interaction would then be larger than the values usually associated with imidoyls.[16-20] Similarly the bridged structure VII cannot be discounted because we do not know what hfi to expect for such a species.

In an attempt to generate authentic organometallic imidoyls, albeit with the metal atom and alkyl radical transposed, group 11 metal atoms were deposited with alkyl isocyanides. Addition would be expected to occur at the carbon atom of the isocyanide function to give $RN{=}\dot{C}M$. However, although reaction was rapid, as judged by the absence of metal atoms, the imidoyls were too unstable to be isolated at 77 K and gave only the alkyl R· formed by β-scission of the imidoyl or cyanoalkyls by H-atom abstraction. This evidence although somewhat circumstantial does suggest that organometallic imidoyls are not formed under our experimental conditions.

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Cu atoms and $(CH_3)_3CCN$ and CH_3CN give two adducts with $\rho_M = 0.14–0.2$ which are similar to two of the species given by Cu atoms and HCN,[3] and the third species formed with HCN is not observed with the alkyl cyanides. These species could be the cis and trans organocopper iminyls $RC(Cu)=\dot{N}$ although we cannot eliminate the possibility that one of them has the bridged structure III or the imidoyl structure II. Interestingly C_6H_5CN, which might be expected to give a rather stable imidoyl, does not give an identifiable adduct with Cu. CH_2CHCN, on the other hand, gives an adduct with a low ρ_M suggesting that it is not an iminyl although its exact structure is difficult to ascertain.

Conclusions. Group 11 metal atoms react with alkyl cyanides at 77 K in a rotating cryostat to give a variety of paramagnetic monoligand π-complexes and adducts. Complex formation can occur with either side-on or end-on bonding between the ligand and metal atom although end-on bonding species are only observed with Ag atoms. We do not detect complexation with more than one ligand in contrast to the situation when Ag atoms are formed by electron capture by Ag^+ in CH_3CN.[21,22] Organometallic iminyls are observed for all the cyanides and metals, and it would appear that organometallic imidoyls are not stable under our experimental conditions. There is tentative evidence for the formation of cis and trans iminyls although a bridged structure for one of the species cannot be ruled out.

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Registry No. $Cu[(CH_3)_3CCN]$, 94801-03-3; $Ag[(CH_3)_3CCN]$ (side-on bonded), 94801-04-4; $Ag[(CH_3)_3CCN]$ (end-on bonded), 94801-05-5; $Au[(CH_3)_3CCN]$, 94801-06-6; $Ag[CD_3CN]$ (side-on bonded), 94801-07-7; $Ag[CD_3CN]$ (end-on bonded), 94801-08-8; $Au[CD_3CN]$, 94801-09-9; $Cu[C_6H_5CN]$, 94801-10-2; $Ag[C_6H_5CN]$, 94801-11-3; Cu[HCN], 94801-12-4; Ag[HCN] (side-on bonded), 94801-13-5; Ag[HCN] (end-on bonded), 94801-14-6; $(CH_3)_3CC(Cu)=\dot{N}$, 94801-15-7; $(CH_3)_3CC(Ag)=\dot{N}$, 94801-16-8; $(CH_3)_3CC(Au)=\dot{N}$, 94801-17-9; $CH_3C(Cu)=\dot{N}$, 94801-18-0; $CD_3C(Ag)=\dot{N}$, 94801-19-1; $CD_3C(Au)=\dot{N}$, 94801-20-4; $C_6H_5C(Ag)=\dot{N}$, 94801-21-5; $C_6H_5C(Au)=\dot{N}$, 94801-22-6; CH_2CHCN/Cu, 94801-23-7; CH_2CHCN/Ag, 94801-24-8; CH_iCHCN/Au, 94801-25-9.

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C–H Activation. Synthesis of Silyl Derivatives of Niobocene and Tantalocene Hydrides, Their H/D Exchange Reactions with C_6D_6, and the Structure of $Cp_2Ta(H)_2SiMe_2Ph$

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Cp_2MH_3 (M = Nb, Ta) reacts with $PhMe_2SiH$ to give $Cp_2M(H)_2SiPhMe_2$. Cp_2NbH_3 reacts with pentamethyldisiloxane to give partial conversion to $Cp_2Nb(H)_2SiMe_2OSiMe_3$, and with Et_3SiH, no Nb silyl complexes were isolated. Cp_2NbH_3 catalyzes H/D exchange between Et_3SiH and C_6D_6 and produces deuterated $[Cp(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)HNb]_2$, as the major organometallic product. Some general conclusions regarding productive activation of C–H bonds are drawn. The molecular structure of $Cp_2Ta(H)_2SiMe_2Ph$ was determined by X-ray crystallography: space group $P\bar{1}$, $a = 7.856\ (2)$ Å, $b = 9.454\ (2)$ Å, $c = 12.257\ (2)$ Å, $\alpha = 97.48\ (2)°$, $\beta = 107.55\ (1)°$, $\gamma = 98.09\ (2)°$, $V = 845.1\ (3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.77$ g/cm^3, $R_1 = 0.036$, $R_2 = 0.046$. The Ta–Si bond length is 2.651 (4) Å. Details of the ^1H NMR and the ^{93}Nb NMR of Cp_2NbH_3 are also reported.

Introduction

Activation of the C–H bond by transition-metal complexes is currently an area of intense research activity, and several important advances in this area have recently been reported.[1-3] In spite of the intense activity in this area, *productive* activation of the C–H bond by organometallic complexes is still a rare phenomenon. By a productive activation, we refer to a process wherein the hydrogen atom bonded to carbon is replaced with another functionality (this excludes H/D exchange) (eq 1). We are aware of only

$$C–H + X–Y \rightarrow C–X + H–Y \qquad (1)$$

three examples of eq 1 being effected by discrete metal complexes in a homogeneous medium,[4] viz., eq 2–4.[1,3i,5]

$$PhH + Et_3Al \xrightarrow{Cp_2NbH_3} Ph–AlEt_2 + Et–H \qquad (2)$$

$$PhH + CO \xrightarrow[h\nu]{(dppe)Ir(CO)H_3} PhCHO \qquad (3)$$

$$PhH + HSiR_3 \xrightarrow{L_2Ir(CO)Cl} Ph–SiR_3 + H_2 \qquad (4)$$

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