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^{13}C NMR Studies of the Carbamoyl Ligand in Organotransition Metal Complexes

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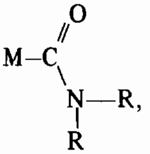
Organometallic complexes containing carbamoyl ligands,



where R = H or alkyl and M = a transition metal, were first prepared and studied in some detail [1, 2] before ^{13}C NMR spectrometry was generally available. Thus, despite the fact that a substantial number of carbamoyl complexes are known, very few ^{13}C NMR data for these complexes have been reported. A recent ^{13}C NMR compilation [3] cites no carbamoyl results. We are aware of ^{13}C data for only 4 transition metal carbamoyl compounds [4–6] plus an organothorium complex [7]. The recent interest [6, 8–10] in cluster complexes containing carbamoyl ligands and the possible usefulness of ^{13}C NMR spectrometry for detecting the carbamoyl group in them led us to examine ^{13}C NMR resonances of the C atom in a variety of known and well-characterized carbamoyl complexes.

Experimental

The following compounds were prepared according to literature procedures: $CpW(CO)_3[C(=O)\overline{N(CH_2)_4CH_2}]$ [11], $CpFe(CO)_2[C(=O)NHC_6H_{11}]$ [12], $CpFe(CO)_2[C(=O)NHMe]$ [12], $CpFe(CO)_2[C(=O)\overline{N(CH_2)_4CH_2}]$ [12], *cis*-$Re(CO)_4(NH_2Me)[C(=O)NHMe]$ [13], $CpFe(CO)(PPh_3)[C(=O)NHMe]$ [12], $Hg[C(=O)NEt_2]_2$ [14], and *cis*-$Mn(CO)_4(NH_2Me)[C(=O)NHMe]$ [15].

Preparation of $CpFe(CO)(PMe_2Ph)[C(=O)NHMe]$

The $[CpFe(CO)_3]CF_3SO_3$ starting material was prepared following the procedure in reference [12] using CF_3SO_3H instead of gaseous HCl. Following the procedure [16] for the preparation of other $CpFe(CO)_2(L)^+$ complexes, $[CpFe(CO)_2(PMe_2Ph)]CF_3SO_3$ was prepared by adding dropwise 7.0 mmol of PMe_2Ph in 25 ml of acetone to a solution of 1.26 g (3.55 mmol) of $[CpFe(CO)_3]CF_3SO_3$ in 15 ml of acetone at 0 °C under an N_2 atmosphere. Progress of the reaction was monitored by IR to avoid formation of $CpFe(CO)(PMe_2Ph)_2^+$ and to maximize the amount of the desired product. The solvent was evaporated under vacuum, and the residue was washed several times with Et_2O. It was then recrystallized from CH_2Cl_2/Et_2O to give 1.73 g (86.6%) of yellow crystalline $[CpFe(CO)_2(PMe_2Ph)]CF_3SO_3$. *Anal.* Found: C, 41.23; H, 3.43%. Calcd.: C, 41.39; H, 3.45%. IR(CH_2Cl_2), ν(CO): 2058s, 2015s cm^{-1}. ^{13}C NMR ($CDCl_3$): δ208.9 ppm doublet, CO, J(CP) = 23.4 Hz; 87.5 singlet, Cp; 18.6 doublet, Me, J(CP) = 35.2. To produce the carbamoyl complex, $MeNH_2$ was bubbled through a stirred mixture of $[CpFe(CO)_2(PMe_2Ph)]CF_3SO_3$ (0.203 g, 0.437 mmol) in 30 ml of Et_2O at 0 °C until the complex had dissolved. Then, 0.5 g of NaH was added to drive to completion the formation of the carbamoyl complex by liberating H_2. After being stirred for 4 hours, the solution was filtered, and the filtrate was evaporated to dryness. The residue was extracted with Et_2O and was recrystallized from Et_2O/pentane at –70 °C to give $CpFe(CO)(PMe_2Ph)[C(=O)NHMe]$ in 30% (0.046 g) yield. The IR spectrum of this compound in CH_2Cl_2 solvent in the ν(CO) region shows one band at 1907s cm^{-1} for the CO and one at 1574w cm^{-1} for the carbamoyl ν(C=O); these values are very similar to those reported [12] previously for $CpFe(CO)(PPh_3)[C(=O)NHMe]$.

^{13}C NMR Spectra

Proton-decoupled ^{13}C spectra were recorded on a JEOL FX-900 spectrometer. Typically, 30,000 accumulations were obtained on a 30 mg carbamoyl compound sample in a 5 mm sample tube also containing approximately 3 mg of $Cr(acac)_3$ relaxation reagent [17], tetramethylsilane (TMS) internal standard, and 0.25 ml of the N_2-saturated solvent.

Results and Discussion

In Table I, the compounds (including those from the literature) are listed in order of increasing ^{13}C chemical shift (δ) for the carbamoyl carbon atom. The 3 compounds with both C and O atoms bonded to metals are given at the bottom. As the carbamoyl

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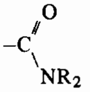
TABLE I. ^{13}C NMR Data for Carbamoyl Complexes.[a]

Compound	 $-C(=O)NR_2$	CO
$CpW(CO)_3[C(=O)\overline{N(CH_2)_4CH_2}]$	183.0	226.7[b], 219.3
$CpFe(CO)_2[C(=O)NHC_6H_{11}]$	193.0	214.4
$CpFe(CO)_2[C(=O)\overline{N(CH_2)_4CH_2}]$	194.7	214.1
$CpFe(CO)_2[C(=O)NHMe]$	195.2	214.3
cis-$Re(CO)_4(NH_2Me)[C(=O)NHMe]$	200.6	190.5, 190.3, 189.5[c]
$Fe(CO)_4[C(=O)NMe_2]^-$	206.0[d]	221.1[d]
$CpFe(CO)(PPh_3)[C(=O)NHMe]$	210.0[e]	220.7[f]
$CpFe(CO)(PMe_2Ph)[C(=O)NHMe]$	211.1[f]	220.0[g]
$Hg[C(=O)NEt_2]_2$	211.1	
$[CpFe(CO)[C(=O)NH_2](Ph_2PCH_2)]_2$	214.9[h]	220.3[h]
cis-$Mn(CO)_4(NH_2Me)[C(=O)NHMe]$	217.9	214.0[i], 213.0[i], 211.1
$(h\text{-}Me_5C_5)_2Th[h^2\text{-}C(=O)NEt_2]Cl$	248.5[j]	
$Ru_3[\mu\text{-}C(=O)NMe_2](CO)_{10}^-$	210.6[k]	
$Os_3[\mu\text{-}C(=O)NMe_2](CO)_{10}^-$	189.0[k]	

[a] In $CDCl_3$ solvent unless otherwise noted. Chemical shifts in w ppm units downfield from TMS. [b] The CO group *trans* to the carbamoyl ligand. [c] Approximate relative intensities are 1:1:2. [d] From reference 5. In CD_3CN at room temperature. [e] Doublet, J(CP) = 27.3 Hz. [f] Doublet, J(CP) = 31.3 Hz. [g] Doublet, J(CP) = 33.2 Hz. [h] From reference 4. In d_6-acetone solvent at –30 °C. [i] Broad and overlapping. [j] From reference 7. [k] From reference 6. In THF at –95 °C. The $-C(=O)NMe_2$ group bonds to two metal atoms *via* the C and O atoms.

resonance occurs in the same region as the carbonyl ligands, it is appropriate to comment on the assignments made in the Table. The assignments for $CpW(CO)_3[C(=O)\overline{N(CH_2)_4CH_2}]$ are based on the relative intensities of the absorptions and the commonly observed range of δ values for CO ligands in $CpW(CO)_3X$ complexes [3]. Assignments for the $CpFe(CO)_2[C(=O)NR_2]$ compounds are based on relative intensities. In the phosphine-substituted complexes $CpFe(CO)(PR_3)[C(=O)NHMe]$, it is assumed that the CO resonance will be at lower field than in $CpFe(CO)_2[C(=O)NHMe]$; this trend in CO chemical shifts is very commonly observed in phosphine–carbonyl systems [3, 18–22]. This requirement demands the assignments in the Table, which is also consistent with assignments [23] made for the pair of compounds $CpFe(CO)_2[C(=O)Me]$ and $CpFe(CO)PPh_3[C(=O)Me]$. Based on these arguments, it appears that the resonances in $[CpFe(CO)[C(=O)NH_2](Ph_2PCH_2]_2$ were misassigned [4] and have been reassigned in Table I. The absorptions in *cis*-$Re(CO)_4(NH_2Me)[C(=O)MHMe]$ are assigned on the basis of relative intensities and the observation that the CO ligands in $Re(CO)_5X$ compounds are commonly found [3] in the range 175–190 ppm. Assignments for the analogous manganese complex *cis*-$Mn(CO)_4(NH_2Me)[C(=O)NHMe]$ are the most difficult to make because of the small chemical shift range observed. All resonances are in the range for $Mn(CO)_5X$ compounds [3]. By analogy with the Re complex, we tentatively assign the lowest field resonance to the carbamoyl carbon.

There are several observations that might be made based on the data in Table I.

1. The carbamoyl carbon resonances fall in the rather narrow range of δ 183–218 ppm for all compounds except for the η^2-carbamoyl complex of thorium.

2. The carbamoyl chemical shift is affected only modestly by changes in the NR_2 group as indicated by the series of compounds $CpFe(CO)_2[C(=O)NR_2]$, where $NR_2=NHC_6H_{11}$ (193.0 ppm), $\overline{N(CH_2)_4CH_2}$ (194.7), and NHMe (195.2).

3. In comparable compounds where data are available, the carbamoyl carbon is at 60–72 ppm higher field than the corresponding acetyl carbon. This trend can be seen in the following pairs of compounds: $CpFe(CO)_2[C(=O)NHMe]$ (195.2 ppm) *vs.* $CpFe(CO)_2[C(=O)Me]$ (254.4) [23]; $CpFe(CO)(PPh_3)[C(=O)NHMe]$ (210.0 ppm) *vs.* $CpFe(CO)(PPh_3)[C(=O)Me]$ (277.0) [23]; $Fe(CO)_4[C(=O)NMe_2]^-$ (206.0 ppm) *vs.* $Fe(CO)_4[C(=O)Me]^-$ (277.2) [24].

4. The replacement of a CO ligand by a phosphine shifts the carbamoyl carbon resonance to lower field, a trend which is also observed for CO ligands [3,

18–22]. This is seen in the comparison of $CpFe(CO)_2[C(=O)NHMe]$ (195.2 ppm) with $CpFe(CO)(PPh_3)[C(=O)NHMe]$ (210.0) and $CpFe(CO)(PMe_2Ph)[C(=O)NHMe]$ (211.1). These data also indicate that the carbamoyl chemical shift is not very sensitive to the particular phosphine (PPh_3 or PMe_2Ph) involved.

5. There appears to be no general correlation between the chemical shifts of the carbamoyl and CO groups in compounds with different metal atoms. Limited correlations, as for the $CpFe(CO)(L)[C(=O)NHMe]$ series with varying L groups, may be expected.

6. In comparable compounds, the chemical shift of the carbamoyl carbon is greater for the complex having the lighter metal. For example, for $M(CO)_4(NH_2Me)[C(=O)NHMe]$, Mn (217.9 ppm) > Re (200.6); and for $M_3[\mu\text{-}C(=O)NMe_2](CO)_{10}^-$, Ru (210.6 ppm) > Os (189.0). This trend has also been observed in metal carbonyl complexes [3, 18–22, 25].

These observations may be use in assigning ^{13}C NMR resonances in new carbamoyl complexes.

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