Notes

Co-ordination Kinetics of Some Aliphatic Amines towards the Photogenerated Transient 'CoH{PPh(OEt)$_2$}$_3$'

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Time-resolved absorption spectra were observed after nitrogen-laser flash photolysis of toluene solutions of [$CoHL_4$] [L = PPh(OEt)$_2$] in the presence of some aliphatic amines, and second-order rate constants were evaluated for co-ordination of the amines to the co-ordinatively unsaturated transient '$CoHL_3$' photogenerated. The steric bulk of substituents on the amine nitrogens is a dominant factor in the magnitude of the constants. The $CoHL_3$(amine) adducts were also formed upon continuous photolysis with a high-pressure mercury lamp, and found to be stable at temperatures lower than −40 °C, on the basis of their ^{31}P n.m.r. and visible absorption spectra.

The photochemistry of organometallic complexes continues to be an active area of research,[1] and much effort has been focused on the properties of the nascent photoproducts,[2] involving co-ordinatively unsaturated organometallic species with high catalytic activities.[3,4] The usefulness of pulsed-laser photolysis has been realized in the investigation of the chemical reactivities of these photoproducts and the kinetics of their subsequent reactions.[5]

We have reported that photoirradiation of tetrakis(diethyl phenylphosphonite)hydridocobalt(I) [$CoHL_4$] [L = PPh(OEt)$_2$] induces the dissociation of PPh(OEt)$_2$ to give a transient hydridocobalt(I) species '$CoHL_3$,'[4,6] which catalyzes double-bond migration of olefins and hydrogen transfer from secondary alcohols to ketones.[4,7] From the analysis of time-resolved absorption spectra observed after laser flash photolysis, second-order rate constants have been obtained for co-ordination of olefins and PPh(OEt)$_2$ to the photogenerated $CoHL_3$.[4,6] The present Note deals with the comparative study of the co-ordination kinetics for some classes of aliphatic amines towards $CoHL_3$, and the properties of the $CoHL_3$(amine) adducts formed.

Results and Discussion

The complex [$CoHL_4$] was photolyzed in the presence of amines at ambient temperature, by use of a nitrogen pulsed laser. The time-resolved absorption spectra showed decay of the two bands at 580 and 760 nm, corresponding to the decrease in concentration of the photogenerated $CoHL_3$ due to recombination with the photodissociated PPh(OEt)$_2$ and to co-ordination of amines. Moreover, a band around 440 nm increased in intensity, attributed to the formation of adducts $CoHL_3$(amine). The spectra exhibited clear isosbestic points, for example at 517 nm in the case of piperidine.

The Table summarizes the second-order rate constants (k') for the co-ordination of aliphatic amines to $CoHL_3$. The value for a primary amine (*i.e.* propylamine) was far larger than those for secondary amines, and further the latter constants were larger than those for tertiary amines. It is noted also that k' values for cyclic amines in the present study were about five times larger than those for the corresponding acyclic chain amines (*e.g.* piperidine *vs.* *N*-ethylpropylamine). These findings indicated that the steric bulk of substituents on nitrogen was a dominant factor in the magnitude of k' for these aliphatic amines.

Table. Co-ordination of amines to photogenerated $CoHL_3$ and ^{31}P n.m.r. data for the $CoHL_3$(amine) adducts formed

		^{31}P N.m.r. of $CoHL_3$(amine) (Continuous photolysis[b])	
Amine	k'/dm^3 mol^{-1} s^{-1} (Flash photolysis)[a]	δ(Adduct)/ p.p.m.	Molar ratio [$CoHL_4$]:[adduct]
NH_2Pr^n	4.7×10^8	170.7	39.5:60.5
$NHEtPr^n$	1.1×10^7	185.9	99.0:1.0
NEt_2Pr^n	1.9×10^4	*c*	—
Piperidine	5.3×10^7	166.9	97.1:2.9
Quinuclidine	1.0×10^5	*c*	—

[a] Second-order rate constants for co-ordination of amines to $CoHL_3$, evaluated from the decay of the transient absorption band ($CoHL_3$) at 580 nm and regarded as accurate to within *ca.* 10%; see ref. 4: $-d[CoHL_3]/dt = k[CoHL_3][L] + k'[CoHL_3][amine]$, where $k = 1.4 \times 10^8$ dm^3 mol^{-1} s^{-1}. [b] Photolysis of [$CoHL_4$] with a 30-fold molar excess of amine in [$^2H_8$]toluene at −70 °C for 4 h; n.m.r. spectra measured at −70 °C. [c] Signals due to adduct formation were not observed.

Moreover, the complex [$CoHL_4$] with amines was subjected to continuous photolysis with a high-pressure mercury lamp. In a typical photolysis at −70 °C, we irradiated a [$^2H_8$]toluene solution of [$CoHL_4$] and propylamine in a molar ratio of 1:5200. The ^{31}P n.m.r. spectrum observed at the same temperature gave new signals at δ 170.7 for $CoHL_3(NH_2Pr^n)$ and at δ 151.5 for the photodissociated PPh(OEt)$_2$, whereas the signal at δ 174.7 for [$CoHL_4$] disappeared.† The differential absorption spectrum of the solution at −70 °C showed a band at *ca.* 440 nm, consistent with the above-described transient spectra after the pulsed-laser photolysis. The absorption coefficient ε_{440} of $CoHL_3(NH_2Pr^n)$ was estimated to be about 1 970 dm^3 mol^{-1} cm^{-1}.

The $CoHL_3$(amine) adducts were stable at temperatures lower than −40 °C, and reconverted into [$CoHL_4$] upon

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† The magnetic equivalence of the phosphorus ligands in each cobalt(I) species was brought about by rapid intramolecular rearrangement of the five-co-ordinate structure. For similar examples, see J. P. Jesson and E. L. Muetterties, in 'Dynamic Magnetic Resonance Spectroscopy,' eds. L. M. Jackman and F. A. Cotton, Academic Press, New York, 1975, p. 253.

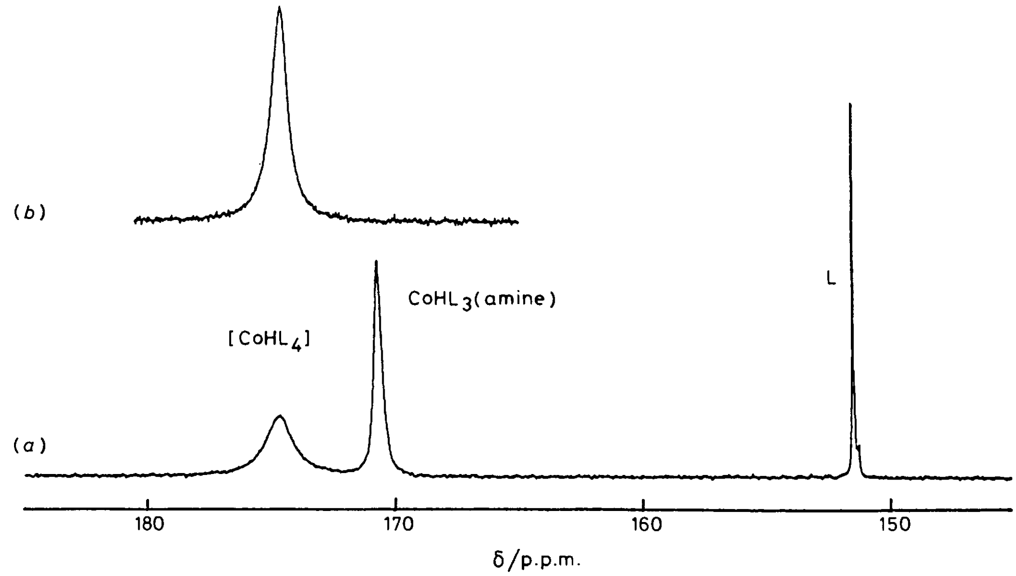

Figure. ^{31}P-{^{1}H} N.m.r. spectra of the CoHL$_3$(NH$_2$Pr^n) adduct measured at −70 °C in [^{2}H$_8$]toluene; [NH$_2$Pr^n]/[CoHL$_4$] = 30. (*a*) The solution after continuous photolysis for 4 h at −70 °C; (*b*) after additional standing of the photoirradiated solution at 10 °C for 5 min

warming to room temperature, indicating the reversibility of PPh(OEt)$_2$ photodissociation from [CoHL$_4$] and displacement of amine in the adducts by the photodissociated PPh(OEt)$_2$ [equation (1), L = PPh(OEt)$_2$].* In the case of the [CoHL$_4$] solutions with a 30-fold molar excess of amine, continuous photolysis at −70 °C gave mixtures of [CoHL$_4$] and CoHL$_3$(amine) at the photoassisted equilibrium (Figure), and the propylamine adduct was formed in higher yield than those with secondary or tertiary amines (Table).

$$[\mathrm{CoHL_4}] + \mathrm{amine} \overset{h\nu}{\rightleftharpoons} \mathrm{CoHL_3(amine)} + \mathrm{L} \quad (1)$$

As a whole, the present Note reveals the importance of the steric bulk of the substituents on nitrogen in co-ordination of aliphatic amines to co-ordinatively unsaturated organometallic transients.

Experimental

The complex [CoHL$_4$][8] and *NN*-diethylpropylamine[9] were prepared by the literature methods, and other amines were commercially available. Test solutions of [CoHL$_4$] and amines in toluene or its deuteriated form were deaerated by bubbling with argon or by several freeze–pump–thaw cycles.

Details of the experimental pulsed-laser procedures have been described previously.[4,10]

For continuous irradiation, a high-pressure mercury lamp (400 W) was used with a Pyrex filter. Phosphorus-31 n.m.r. spectra were obtained on a JEOL-GX-400 spectrometer, and were referenced to external P(OMe)$_3$ (δ 140 p.p.m. relative to 85% H$_3$PO$_4$). Visible absorption spectra were obtained on a Hitachi 323 spectrometer.

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References

1 G. L. Geoffroy and M. S. Wrighton, 'Organometallic Photochemistry,' Academic Press, New York, 1979; J. J. Zuckerman, 'Inorganic Reactions and Methods,' VCH Verlagsgesellschaft, Weinheim, 1986, vol. 15, ch. 13.
2 See, for example, W. D. Jones and F. J. Feher, *J. Am. Chem. Soc.*, 1984, **106**, 1650; H. L. Conder, A. R. Courtney, and D. DeMarco, *ibid.*, 1979, **101**, 1606; A. S. Goldman and D. R. Tyler, *ibid.*, 1986, **108**, 89; K. A. Mahmoud, A. J. Rest, and H. G. Alt, *J. Chem. Soc., Dalton Trans.*, 1984, 187; H. van der Heijden, A. G. Orpen, and P. Pasman, *J. Chem. Soc., Chem. Commun.*, 1985, 1576.
3 M. J. Mirbach, M. F. Mirbach, A. Saus, N. Topalsavoglou, and T. N. Phu, *J. Am. Chem. Soc.*, 1981, **103**, 7590; M. A. Schroeder and M. S. Wrighton, *ibid.*, 1976, **98**, 551.
4 M. Onishi, S. Oishi, M. Sakaguchi, I. Takaki, and K. Hiraki, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3925 and refs. therein.
5 D. Wink and P. C. Ford, *J. Am. Chem. Soc.*, 1985, **107**, 1794; T. R. Fletcher and R. N. Rosenfeld, *ibid.*, 1986, **108**, 1686; J. R. Winkler, D. G. Nocera, and T. L. Netzel, *ibid.*, p. 4451; T. A. Seder, S. P. Church, and E. Weitz, *ibid.*, p. 4721; W. H. Breckenridge and G. M. Stewart, *ibid.*, p. 364; S. P. Church, F. W. Grevels, H. Hermann, and K. Schaffner, *J. Chem. Soc., Chem. Commun.*, 1985, 30.
6 M. Onishi, K. Hiraki, M. Matsuda, and T. Fukunaga, *Chem. Lett.*, 1983, 261; S. Oishi, K. Tajime, A. Hosaka, and I. Shiojima, *J. Chem. Soc., Chem. Commun.*, 1984, 607.
7 S. Oishi, *J. Mol. Catal.*, 1987, **40**, 289.
8 D. Titus, A. A. Orio, and H. B. Gray, *Inorg. Synth.*, 1977, **13**, 117.
9 N. J. Leonard, F. M. Kraft, and V. Wolfman, *J. Am. Chem. Soc.*, 1948, **70**, 866.
10 S. Oishi, *J. Organomet. Chem.*, 1987, **335**, 207.

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* After continuous photolysis, we detected only a small amount of free PPh(OEt)$_2$ formed through some decomposition of [CoHL$_4$]. There were no other by-products (such as ammonia and olefins), on the basis of gas chromatography.