Rearrangement of Metal-stabilised Carbocations containing Cyclopropyl and Other Alkyl Groups to give Cyano- and Isocyano-complexes: Reactions of Group VI Metal Isocyano-complexes with Nucleophiles

By **Joseph A. Connor** * and **E. Malcolm Jones**, Department of Chemistry, The University, Manchester M13 9PL

The preparation of a series of cyclopropylcarbene complexes $[(CO)_5Cr\{C(X)C_3H_5\}]$ (X = OH, OMe, or NH_2) is reported. The spectroscopic properties (particularly proton n.m.r.) of these complexes show no evidence of stabilisation of the carbocationic site by the cyclopropyl group. Formation of acetoxy-carbene complexes in the reaction between the salts $[(CO)_5Cr\{C(O^-NMe_4^+)Y\}]$ (Y = CH_2SiMe_3 or C_3H_5) and acetyl chloride is inferred from their further reaction with hydrogen azide which gives rise to $[(YNC)Cr(CO)_5]$ and $[(YCN)Cr(CO)_5]$. The mechanism of the reaction is discussed and it is suggested that migration of the group Y from the carbon to the nitrogen atom in a common intermediate $[(CO)_5MC(N)Y]$ will occur most readily when there is little or no stabilisation of the carbocation, through a vertical process, by the group Y. The complex [(cyclopropyl isocyanide)Cr-$(CO)_5$] has been fully characterised. The preparation and characterisation of [(acetyl isocyanide)Cr$(CO)_5$] is described and the presence of extensive conjugation between the isocyano- and the carbonyl group is established. The acetyl isocyanide ligand is rapidly solvolysed by methanol giving $[(HNC)Cr(CO)_5]$ and methyl acetate. When the complex $[(Me_3CNC)Cr(CO)_5]$ is treated with n-butyl-lithium and subsequently alkylated the sole product is the complex *cis*-$[(CO)_4(Me_3CNC)Cr\{C(OEt)Bu\}]$ resulting from nucleophilic attack at a carbonyl rather than the isocyano-ligand.

MUCH recent work on transition-metal carbene complexes [1] has examined the role of various substituents in stabilising the carbene carbon atom in these systems which are best regarded as metal-stabilised carbocations.[2] The contribution of vertical stabilisation [3] to the bonding in complexes of the type $[(CO)_5Cr\{C(X)Y\}]$, as indicated by their physical and chemical properties, has been examined [4] in a variety of complexes containing different organic substituents, Y. The cyclopropyl ring, which can act both as a π-acid and a π-base,[5] is known to interact strongly with adjacent carbocationic centres [6] by a vertical mechanism.[3] We have prepared a series of cyclopropylcarbene complexes, $[(CO)_5Cr\{C(X)C_3H_5\}]$ (X = OH, OMe, $O^-NMe_4^+$, or NH_2), and examined some of their reactions.

The reaction between an acyloxy-carbene complex and hydrogen azide to give a cyano-complex as a result of a concerted rearrangement has been described.[7] We have explored this general reaction and find that in certain cases the corresponding isocyano-complex is also formed. This type of rearrangement is of special interest in relation to recent studies on models of the nitrogenase enzyme system.[8]

RESULTS AND DISCUSSION

The cyclopropyl complexes were prepared by standard methods.[1] The hydroxy-carbene complex $[(CO)_5Cr\{C(OH)C_3H_5\}]$ is particularly sensitive to heat and light. The spectroscopic properties of the complexes are generally in accord with expectation; thus the stretching frequency, $\nu(CO)A_1'$, of the carbonyl group *trans* to the carbene ligand $\{C(X)C_3H_5\}$ decreases in the order X = OH > OMe > NH_2 > $O^-NMe_4^+$, which is consistent with increasing electron donation from X in the reverse order. The electronic spectra of the complexes do not indicate any difference between the cyclopropyl group and an alkyl group in a similar system.[9] There is no evidence of conjugation between the cyclopropyl ring and the carbocationic centre (*cf.* refs. 4 and 7).

A detailed examination of the proton n.m.r. spectra of the complexes $[(CO)_5Cr\{C(X)C_3H_5\}]$ (X = $O^-NMe_4^+$, NH_2, or OMe) showed a number of unusual features. The signals from the methine proton (H_1) are observed at low field compared with those of most other monosubstituted cyclopropanes [10-11] (Table). This reflects the strong electron-withdrawing properties of the $(CO)_5CrC(X)$ group.[4] The chemical shifts of the methylene protons $H_{2,4}$ and $H_{3,5}$ were assigned [$\delta(H_{3,5}) > \delta(H_{2,4})$] on the basis of comparison with other monosubstituted cyclopropanes [11] and follow H_1 in their dependence on the heteroatom substituent X. By analogy with acyl cyclopropanes [12] the cyclopropyl ring may adopt either of two conformations [(*a*),(*b*)] relative to the Cr–C(carbene) bond in these complexes. The aromatic-solvent induced (ASI) shifts [4a] of the protons $H_{2,4}$ is greater than that of $H_{3,5}$ in the complexes $[(CO)_5Cr\{C(X)C_3H_5\}]$ (X = OMe or NH_2). This is consistent with the latter set of protons being

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[1] D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

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[3] T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5715.

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[5] A. H. Cowley, J. L. Mills, T. M. Loehr, and T. V. Long, *J. Amer. Chem. Soc.*, 1971, **93**, 2150.

[6] G. A. Olah, C. L. Juell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, 1972, **94**, 146.

[7] J. A. Connor and E. M. Jones, *J. Chem. Soc.* (*A*), 1971, 3368.

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[12] M. Pelissier, A. Serafini, J. Devanneaux, J. F. Labarre, and J. F. Tocanne, *Tetrahedron*, 1971, **27**, 3271; L. S. Bartell, B. L. Carroll, and J. P. Guillory, *Tetrahedron Letters*, 1964, 705; E. M. Kosower and M. Ito, *Proc. Chem. Soc.*, 1962, 25.

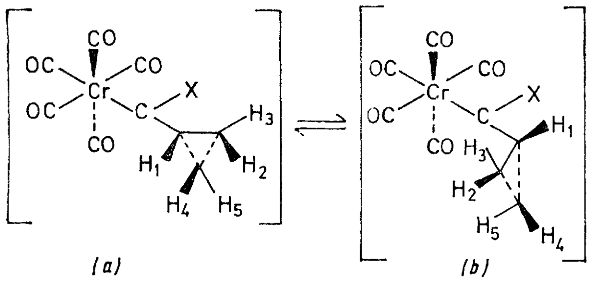
closer to the group X and $Cr(CO)_5$ respectively in the two conformations. The proton spectrum of the cyclopropyl group of the complex $[(CO)_5Cr\{C(NH_2)C_3H_5\}]$ in $[^2H_6]$-acetone solution appears as a quintet (J 7 Hz) (H_1) and a doublet (J 7 Hz) ($H_{2,4}$; $H_{3,5}$). This is in sharp contrast to the spectra of the other complexes in the same solvent and of all three complexes in $[^2H_6]$benzene which appear generally as a nine-line methine and a twenty-line methylene proton signal.

Proton chemical shifts (δ p.p.m.) and coupling constants (J/Hz) in cyclopropyl compounds, C_3H_5X

X	Solvent [a]	$\delta(H_1)$	$\delta(H_{2,4})$	$\delta(H_{3,5})$	$^3J_{12,14}$	$^3J_{13,15}$	$^3J_{24}$	$^3J_{35}$	$^3J_{25,34}$	$^2J_{23,45}$	Ref.
COMe	Neat	1·95	0·81	0·85	7·87	4·64	9·06	9·60	6·94	−3·48	*b*
NH_2	Neat	2·22	0·32	0·20	6·63	3·55	9·60	9·96	6·18	−4·29	*b*
OH	1	3·35	0·34	0·59	6·19	2·94	10·27	10·88	6·84	−5·43	11
F	1	4·32	0·27	0·69	5·89	2·39	10·80	12·01	7·70	−6·69	11
Br	Neat	2·83	0·81	0·96	7·13	3·80	10·16	10·54	7·01	−6·12	*b*
	Neat	2·83	0·83	0·98	6·83	3·85	10·49	10·92	7·14	−5·88	*c*
$(CO)_5CrC(O^-NMe_4^+)-$	2	2·79	0·31	0·66	7·67	4·56	6·04	6·04	2·86	−6·59	*c*
$(CO)_5CrC(NH_2)-$	2	2·76	1·17	1·17							*c*
	1	2·19	0·33	0·57	7·24	5·59	7·02	5·54	3·19	−7·77	*c*
	3	2·81	1·18	1·27							*c*
$(CO)_5CrC(OMe)-$	2	3·51	1·25	1·42	7·64	4·45	5·79	5·87	3·70	−6·80	*c*
	1	3·18	0·60	0·94							*c*
	3	3·48	1·28	1·28							*c*
$(CO)_5CrC(OH)-$	2	3·49	1·20	1·37	7·20	4·80					*c*
$(CO)_5CrCN-$	2	3·23	1·10	1·10	6·60	4·10					

[a] 1, C_6D_6; 2, $(CD_3)_2CO$; 3, $CDCl_3$. [b] K. M. Crecely, V. S. Watts, and J. H. Goldstein, *J. Mol. Spectroscopy*, 1969, **30**, 184. [c] This work.

The five-spin AA'BB'X spectrum of these cyclopropyl complexes $[(CO)_5Cr\{C(X)C_3H_5\}]$ (X = OMe, NH_2, or $O^-NMe_4^+$) was analysed with the aid of the iterative computer program LAOCN 3,[13] together with a non-iterative n.m.r. simulation program for a five-spin system.[14] Both programs were tested by analysing the spectrum of C_3H_5Br. This gave results in good agreement with literature values.[10] The results of these analyses are presented in the Table together with a selection of results taken from the literature. Coupling constants $J_{12,14}$ and $J_{13,15}$ for each of the three complexes are similar to those typical of cyclopropyl ketones, rather as would be expected from the previous discussion. The values of the remaining coupling constants, J_{ij} ($i \neq j$ = 2—5), that is those couplings which involve the methylene protons *only*, are remarkably different from those of any other cyclopropyl compound for which information is available, being reduced by 3—4 Hz (that is, by *ca.* 50%) in each case.



(a) (b)

As the figures in the Table show, values of J_{ij} ($i \neq j$ = 1—5) in many monosubstituted cyclopropanes vary in an approximately linear manner with the electronegativity of the substituent.[11,15] Such a correlation would predict high values for $^3J_{ij}$ ($i \neq j$ = 2—5) rather than the low values found. The dependence of $^3J_{HH}$ on the dihedral angle can be expressed in terms of the Karplus equation.[16] When this is applied to the values of $^3J_{ij}$ ($i \neq j$ = 2—5) in the cyclopropylcarbene complexes, a distortion of 30 ± 10° would appear necessary to accommodate the observations. Such an explanation is particularly unacceptable in such a rigid ring system.

Reaction with Acids.—A number of attempts to prepare the acetoxy-complex $[(CO)_5Cr\{C(OAc)C_3H_5\}]$ from the reaction [7] between acetyl chloride and the salt $[(CO)_5Cr\{C(O^-NMe_4^+)C_3H_5\}]$ were unsuccessful. Instead the salt $Me_4N[(CO)_5CrCl]$ was obtained. Similar behaviour has been observed for the salt $[(CO)_5Cr\{C(O^-NMe_4^+)CH_2SiMe_3\}]$ and evidence was obtained for the intermediacy of $[Cr(CO)_5]$ in this reaction.[4c] That an acetoxy-complex $[(CO)_5Cr\{C(OAc)Y\}]$ (Y = CH_2SiMe_3 or C_3H_5) is indeed formed in both systems was established in the following manner.

When hydrogen azide was added to a mixture of the salt $[(CO)_5Cr\{(CO^-NMe_4^+)C_3H_5\}]$ and acetyl chloride in methylene chloride solution the major product was the isocyano-complex $[(CO)_5Cr(CNC_3H_5)]$. The isomeric cyano-complex was also formed, albeit in small amounts (isocyanide : cyanide > 20 : 1). This reaction is clearly similar to that which was observed between hydrogen azide and the fully characterised acetoxy-complex $[(CO)_5Cr\{(OAc)C_4H_3O\}]$, which leads by way of the unstable azido-intermediate $[(CO)_5Cr\{C(N_3)C_4H_3O\}]$ to the 2-furyl cyanide complex $[(CO)_5Cr(NCC_4H_3O)]$.[7] When hydrogen azide was added to a mixture of acetyl chloride and the salt $[(CO)_5Cr\{C(O^-NMe_4^+)CH_2SiMe_3\}]$ in methylene chloride the products were the methyl isocyanide complex $[(CO)_5Cr(CNMe)]$ and the isomeric cyano-complex $[(CO)_5Cr(NCMe)]$ in the ratio 4 : 1 respectively. This is clearly consistent with the formation of the

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[13] A. A. Bothner-By and S. M. Castellano in 'Computer Programs for Chemistry,' ed. D. F. Detar, Benjamin, New York, 1968.

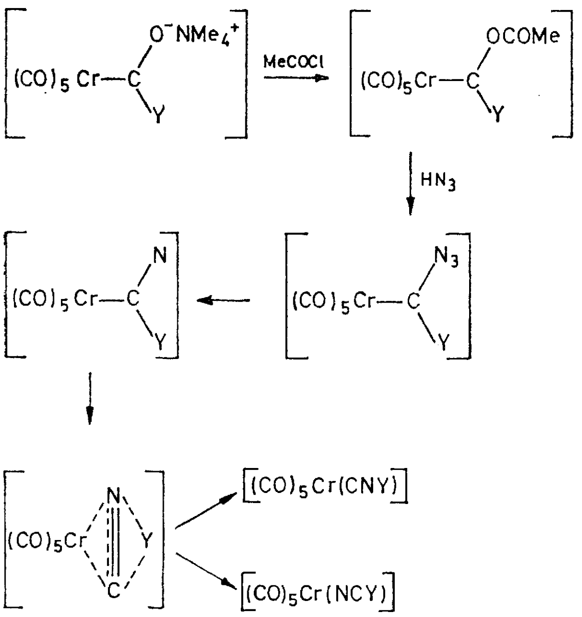
[14] F. Heatley, unpublished work.

[15] T. Schaefer, F. Hruska, and G. Kotowycz, *Canad. J. Chem.*, 1965, **43**, 75.

[16] M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

acetoxy-complex $[(CO)_5Cr\{C(OAc)CH_2SiMe_3\}]$ as an intermediate in the reaction which subsequently reacts with HN_3 to give $[(CO)_5Cr\{C(N_3)CH_2SiMe_3\}]$. We have shown[4c] that HCl does not react with the complex $[(CO)_5Cr\{C(OEt)CH_2SiMe_3\}]$ and consequently prefer to consider that the $Si-CH_2$ bond is broken by acetic acid after the azido-complex has been formed. Such a pattern is consistent with the nucleophilicities of the ions as indicated by the dissociation constants of the acids (pK_a in dmf: HOAc 11·1; HN_3 8·5; and HCl 3·4),[17] which suggest that acetate ion is a stronger nucleophile than azide ion.

The loss of nitrogen from the azido-carbene complex $[(CO)_5Cr\{C(N_3)Y\}]$ [$Y = C_3H_5$, C_4H_3O, or CH_2SiMe_3 (or, more likely, Me)] would give a nitrene-like intermediate $[(CO)_5Cr\{C(N)Y\}]$. We were unable to trap this intermediate with diethyl maleate and this fact, together with the mild conditions of the rearrangement, strongly indicates that the overall process is concerted. Rearrangement of $[(CO)_5Cr\{C(N)Y\}]$ to give the isocyano-complex $[(CO)_5Cr(CNY)]$ is formally analogous to the Schmidt reaction and involves the migration of Y from the carbenium carbon to the nitrene nitrogen atom. The alternative rearrangement to give the cyano-complex $[(CO)_5Cr(NCY)]$, the fulminate analogue, has no counterpart in organic chemistry, and its appearance in the present instance may simply reflect the preference of $[Cr(CO)_5]$ for a nitrogen rather than a carbon donor. The mechanism detailed above is summarised in the Scheme (Y = 2-furyl, Me, or C_3H_5).



SCHEME

The ratio of isocyano- to cyano-complex formed in these reactions increases in the order Y = 2-furyl ($< 0·01$) $<$ Me (4) $< C_3H_5$ (> 20). This order might be interpreted to show that the C(carbene)–Y bond strength decreases from Y = 2-furyl to $Y = C_3H_5$. This in turn is consistent wlth evidence from spectroscopic measurements of a parallel decrease in the amount of vertical (σ–π) stabilisation of the carbocation centre by the group Y in the complexes. A kinetic explanation based on the different electrophilicity of the groups Y cannot be excluded.

When the salt $[(CO)_5Cr\{C(O^-NMe_4^+)C_3H_5\}]$ was treated with hydrogen chloride a rapid reaction gave $Me_4N[(CO)_5CrCl]$ in high yield. However, when HBF_4 was used the product was the hydroxy-carbene complex, $[(CO)_5Cr\{C(OH)C_3H_5\}]$. This is the first hydroxy-carbene complex of a Group VI metal to be isolated, although the rhenium complex $[(\pi\text{-}C_5H_5)(CO)_2Re\{C(OH)Me\}]$ is well known.[18] The failure to observe electrophilic ring opening of the cyclopropyl ring[19] in $[(CO)_5Cr\{C(O^-NMe_4^+)C_3H_5\}]$ is consistent with the strong electron-withdrawing character of the $(CO)_5CrC(O^-NMe_4^+)$ group.

The Complex $[(C_3H_5CN)Cr(CO)_5]$.—Although cyclopropyl isocyanide, C_3H_5NC, is unknown and we were therefore unable to synthesise the complex by an independent route, characterisation of the complex $[(CO)_5Cr(CNC_3H_5)]$ by microanalysis and spectroscopic methods is sufficient for identification, especially against the background of our earlier work.[20] The i.r. spectrum of the complex in the region above 2 100 cm^{-1} shows two weak absorptions at 2 168 and 2 156 cm^{-1} which may be assigned to ν ($-N\equiv C$). The observation of two bands is unusual as all other $[(RNC)Cr(CO)_5]$ complexes[20] show only one band in this region. This anomaly can be explained if the Cr–C–N–C skeleton is not linear. The pattern of carbonyl stretching frequencies leaves no doubt that the complex is of the type $[LCr(CO)_5]$. The n.m.r. spectrum of the complex (Table) is in accord with expectation and provides evidence from $\delta(H_1)$ and $^3J_{1j}$ ($j = 2$—5) of the consequences of σ-donation to the metal *via* the isocyanide carbon atom. The isomeric cyano-complex was obtained in such small quantities that characterisation depends solely on the mass spectrum, which shows a molecular ion and the expected fragmentation pattern, together with a consistent i.r. spectrum in which a very weak band at 2 270 cm^{-1} is assigned to ν($-C\equiv N$), and bands at 2 074w, 1 951vs, and 1 926m cm^{-1} are similar to those found in $[(MeCN)Cr(CO)_5]$.

The Complex $[(MeCONC)Cr(CO)_5]$ *and Reactions of* $[(RNC)Cr(CO)_5]$ *Complexes with Nucleophiles*.—Reaction of the $[(CO)_5CrCN]^-$ ion with Et_3OBF_4 gave the ethyl isocyanide complex $[(EtNC)Cr(CO)_5]$ in good yield. A similar procedure was applied recently to synthesis of $[(\pi\text{-}C_5H_5)(CO)_2Mn(CNEt)]$ from the $[(\pi\text{-}C_5H_5)(CO)_2MnCN]^-$ ion.[21] The reaction between acetyl chloride and $Na[(CO)_5CrCN]$ in methylene chloride solution gave the acetyl isocyanide complex $[(MeCONC)Cr(CO)_5]$ (83%). The preparation of similar complexes $[(RCONC)Cr(CO)_5]$

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[17] B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, 1966, **88**, 1911.

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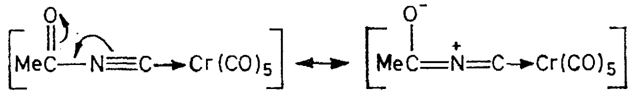
[21] P. J. C. Walker and R. J. Mawby, *J. Chem. Soc.* (*A*), 1971, 3006.

(R = Pr^i, Ph, $PhCH_2$, or PhCH=CH–) has been mentioned in the patent literature,[22] but their characterisation and reactivity have not been described.

The free isocyanide is unknown and all attempts to prepare MeCONC have led to the isomeric cyanide.[23] The isocyano-complex $[(MeCONC)Cr(CO)_5]$ shows ν(–N≡C) at 2 109 cm^{-1} [*cf.* MeCOCN ν (–C≡N) 2 221 cm^{-1} (ref. 24)] which, when compared to that in alkyl isocyanide complexes [20] (*ca.* 2 165 cm^{-1}) suggests extensive conjugation between the –N≡C bond and the carbonyl group in the manner shown below. The consequent decrease in the σ-donor : π-acceptor ratio of the ligand is reflected in a significant increase of the *trans*-CO stretching frequency $\nu(CO)A_1'$, to 1 977 cm^{-1} from its value in alkyl and aryl isocyano-complexes [20] (*ca.* 1 963 cm^{-1}). The ketonic carbonyl stretching frequency of the acetyl group in the complex (1 754 cm^{-1}), when compared to that in MeCOCN [25] (1 740 cm^{-1}), tertiary amides (1 630—1 670 cm^{-1}), and acetyl halides [26] (1 790—1 850 cm^{-1}), provides further support for the delocalisation of the nitrogen lone-pair. Conjugation between the acetyl and the isocyano-group, and the influence of this on the nature of the bonding to the metal atom in the complex, is further supported [20] both by the electronic spectrum of $[(MeCONC)Cr(CO)_5]$, which shows two bands in the region $\lambda > 250$ nm at 282 and 362 nm respectively, and by the observation of a large value (126 Hz) for the ASI shift of the methyl protons. The mass spectrum of the complex shows that each of the ions $[(MeCONC)Cr(CO)_{5-x}]^+$ (x = 0—5) readily loses ketene, CH_2CO, to form $[(HNC)Cr(CO)_{5-x}]^+$.



$$\left[\overset{\overset{\mathrm{O}}{\|}}{\mathrm{MeC}}-\mathrm{N}\equiv\mathrm{C}\rightarrow\mathrm{Cr(CO)_5}\right] \longleftrightarrow \left[\overset{\overset{\mathrm{O^-}}{|}}{\mathrm{MeC}}=\overset{+}{\mathrm{N}}=\mathrm{C}\rightarrow\mathrm{Cr(CO)_5}\right]$$

Our previous work had shown that the alkyl isocyano-complexes $[(RNC)Cr(CO)_5]$ were not attacked by mild nucleophiles such as alcohols,[20] in marked contrast to isocyano-complexes of Pt^{II} [27] and Rh^{I}.[28] Treatment of the complex $[(MeCONC)Cr(CO)_5]$ with methanol in hexane at room temperature gave $MeCO_2Me$ and $[(HNC)Cr(CO)_5]$. There was no evidence for the formation of the complex $[(CO)_5Cr\{C(OMe)NHCOMe\}]$. The reaction of $[(Me_3CNC)Cr(CO)_5]$ with n-butyl-lithium and alkylation of the product with Et_3OBF_4 gave the new carbene complex *cis*-$[(CO)_4(Me_3CNC)Cr\{C(OEt)Bu\}]$ (87%). The only other material isolated from the reaction was unreacted $[(Me_3CNC)Cr(CO)_5]$. This result establishes conclusively the inertness of the isocyano-ligand in complexes of the type $[(RNC)Cr(CO)_5]$ to nucleophilic attack, even by the strongest nucleophiles.

CONCLUSIONS

We have found no evidence that the cyclopropyl ring in carbene complexes of the type $[(CO)_5Cr\{C(X)C_3H_5\}]$ (X = $O^-NMe_4^+$, NH_2, OMe, or OH) stabilises the carbocation site by a vertical (or σ–π) mechanism, in contrast to its behaviour in several pure organic systems such as the cyclopropylcarbinyl [29] and tricyclopropyl carbocations.[30] The reaction of a transition-metal carbene complex salt $[(CO)_5Cr\{C(O^-NMe_4^+)Y\}]$ with acetyl chloride and hydrogen azide at or just below room temperature leads, *via* a supposed nitrene-like intermediate $[(CO)_5Cr\{C(N)Y\}]$, to either the isocyano-complex $[(YNC)Cr(CO)_5]$ or the cyano-complex $[(YCN)Cr(CO)_5]$ or to a mixture of both. This rearrangement is governed by the electronic character of the group Y. Where the carbocation of the salt is strongly stabilised by Y through a vertical process, the $Cr(CO)_5$ group migrates from the carbon to the nitrogen atom and the product is the cyano-complex. Where little or no such stabilisation of the carbocation is present the group Y migrates from the carbon to the nitrogen atom and the isocyano-complex is formed.

The reaction appears to be concerted and to involve participation of the metal so that a symmetrical intermediate between the nitrene-like species and the final product appears reasonable. This is clearly related to the intermediates discussed by Schrauzer *et al.*[8] in their studies on the reaction of cyanides and isocyanides with molybdate–cysteine complexes in the presence of $NaBH_4$ and adenosine triphosphate which gives alkanes.

Isocyano-complexes of Group VI metals can be prepared easily by electrophilic attack on cyano-complexes such as the $[(CO)_5CrCN]^-$ ion, but the isocyano-complexes are inert to attack by nucleophiles. When the ligand is a net π-acceptor, as in $[(MeCONC)Cr(CO)_5]$, solvolysis at the R–NC bond occurs readily and attack upon the isocyanide carbon atom is not observed. Carbanions attack $[(RNC)Cr(CO)_5]$ exclusively at a carbonyl carbon atom *cis* to the isocyano-ligand, as was also observed for $[Ph_3MCr(CO)_5]$ (M = P, As, or Sb).[31]

EXPERIMENTAL

Materials and methods employed have been described in detail in earlier publications.[4,7] In particular, the preparation of the two salts $[(CO)_5Cr\{C(O^-NMe_4^+)Y\}]$ (Y = CH_2SiMe_3 or C_3H_5) is described in ref. 4*c*.

Pentacarbonyl[*cyclopropyl*(*methoxy*)*carbene*]*chromium*.—A solution of Me_3OBF_4 (0·51 g, 3·3 mmol) in acetonitrile was added to a stirred suspension of the complex $[(CO)_5Cr$-

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[22] R. E. Maginn, U.S. Patent 3,136,797 (*Chem. Abs.*, 1964, **61**, 7044f); 3,330,860 (*Chem. Abs.*, 1967, **67**, 99,869h).

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$\{C(O^-NMe_4^+)C_3H_5\}]$ (1·01 g, 3·0 mmol) in acetonitrile at room temperature. After stirring for 0·25 h, the solvent was removed under reduced pressure and the residue was extracted with hexane. The hexane solution was purified by chromatography (silica gel) and the solvent removed under reduced pressure to give the *complex* as a pale orange oil (0·75 g, 91%), m.p. *ca.* 5 °C (Found: C, 43·5; H, 3·3; Cr, 18·6. Calc. for $C_{10}H_8CrO_6$: C, 43·5; H, 2·9; Cr, 18·9%). $\nu_{max.}$: (liq. film) 3 092vw; 3 016m; 1 039s; (hexane) 2 064w; 1 983vw; 1 946s; and 1 959m cm^{-1}. $\lambda_{max.}$/nm (log ε) (hexane) *ca.* 245 (4·72) and 376 (3·85). δ ([$^2H_6$]-acetone) 4·70, ([$^2H_6$]benzene) 3·92, and ($CDCl_3$) 4·62 (O–CH_3) p.p.m. *m/e* (*I*): 276 (10), 248 (3); 220 (6); 192 (7); 164 (24); 136 (100); 91 (10); 41 (28); and 39 (35).

[Amino(cyclopropyl)carbene]pentacarbonylchromium.—Ammonia (from evaporation of liquid ammonia) was allowed to bubble through a stirred solution of the complex $[(CO)_5Cr\{C(OMe)C_3H_5\}]$ (0·20 g, 0·69 mmol) in hexane for a period of 5 min at ice temperature. All volatile material was removed under reduced pressure and the residue extracted with hexane–light petroleum (5 : 1 v/v). Crystallisation of this solution at −20 °C gave the *complex* as yellow needles (0·15 g, 87%), m.p. 73 °C (Found: C, 41·3; H, 2·7; Cr, 19·7; N, 5·8. Calc. for $C_9H_7CrNO_5$: C, 41·3; H, 2·7; Cr, 19·9; N, 5·4%). $\nu_{max.}$: (CS_2) 3 438m; 3 321m; 3 232w (N–H); 3 075vw; 3 000vw; 1 021w (C_3H_5); (hexane) 2 061w; 1 973vw; 1 946s; and 1 930m,sh cm^{-1}. $\lambda_{max.}$/nm (log ε) (hexane) *ca.* 245 (4·30) and 365 (4·06). δ([$^2H_6$]-acetone) 9·05, ([$^2H_6$]benzene) 6·50, and ($CDCl_3$) 8·00 (NH_2) p.p.m. *m/e* (*I*): 261 (23); 233 (5); 205 (4); 177 (13); 149 (33); 121 (100); 91 (8); 78 (11); 41 (138); and 39 (79).

Pentacarbonyl(ethyl isocyano)chromium from $Na[(CO)_5CrCN]$.—A solution of Et_3OBF_4 (0·13 g, 0·69 mmol) in methylene chloride was added to the salt $Na[(CO)_5CrCN]$ (0·16 g, 0·66 mmol)[32] suspended in the same solvent. The mixture was stirred for 3 h after which the solvent was removed under reduced pressure. The residue was extracted with hexane; crystallisation of the extract at −20 °C gave colourless needles of $[(EtNC)Cr(CO)_5]$ (0·13 g, 80%), m.p. 32—33 °C. $\nu_{max.}$ (hexane): 2 164w; 2 065m; and 1 960vs cm^{-1} (identical with a standard sample).[20]

(Acetyl isocyano)pentacarbonylchromium.—Acetyl chloride (0·22 g, 2·60 mmol) was added to a stirred suspension of $Na[(CO)_5CrCN]$ (0·54 g, 2·23 mmol) in methylene chloride. The mixture was stirred for 3 h after which all volatiles were removed under reduced pressure. The residue was extracted with hexane–light petroleum (1 : 1 v/v); crystallisation of the extracts at −20 °C gave pale yellow needles of $[(MeCONC)Cr(CO)_5]$ (0·48 g, 82%), m.p. 56—57 °C (Found: C, 36·6; H, 1·5; Cr, 19·7; N, 5·7. Calc. for $C_8H_3CrNO_6$: C, 36·8; H, 1·2; Cr, 19·9; N, 5·4%). $\nu_{max.}$ (hexane): 2 109w; 2 009w; and 1 977vs cm^{-1}. $\lambda_{max.}$/nm (log ε) 282 (3·87) and 362 (3·64). δ($CDCl_3$) 2·44 p.p.m. *m/e* (*I*): 261 (60); 219 (28); 205 (1); 191 (15); 177 (6); 163 (11); 149 (37); 135 (12); 121 (100); 107 (85); 79 (183); and 78 (100).

Reactions.—$[(CO)_5Cr\{C(O^-NMe_4^+)C_3H_5\}]$ *with acetyl chloride*. Acetyl chloride (0·12 g, 1·50 mmol) was added slowly to a stirred solution of the salt (0·49 g, 1·48 mmol) in methylene chloride at room temperature. A purple colouration[7] was observed immediately which, gradually over 0·5 h, changed to give a yellow solution. All volatile material was then removed under reduced pressure. The residue, which was completely insoluble in hexane and in light petroleum, was extracted with methylene chloride. Precipitation from this solution with pentane gave $Me_4N[(CO)_5CrCl]$ (0·40 g, 90%).[33]

$[(CO)_5Cr\{C(O^-NMe_4^+)C_3H_5\}]$ *with acetyl chloride and hydrogen azide*. Acetyl chloride (0·14 g, 1·80 mmol) was added to a stirred solution of the salt (0·57 g, 1·72 mmol) in methylene chloride followed immediately by the addition of a solution of hydrogen azide in benzene[34] (6·8 cm^3, 0·26N; 1·77 mmol). The mixture was stirred at room temperature for 15 min to give a yellow solution. All volatile materials were removed under reduced pressure and the residue extracted with light petroleum. Crystallisation of the ethereal extract at −20 °C produced yellow crystals (0·33 g, 75%). The mixture was recrystallised from hexane at −20 °C to give a pure sample of *pentacarbonyl(cyclopropyl isocyano)chromium* as pale yellow needles (0·25 g, 56%), m.p. 32—33 °C (Found: C, 41·4; H, 1·9; Cr, 20·5; N, 4·7. Calc. for $C_9H_5CrNO_5$: C, 41·7; H, 1·9; Cr, 20·1; N, 5·4%). $\nu_{max.}$: (liquid film) 3 098vw; 3 009w; 1 036s; (hexane) 2 168w; 2 156w; 2 063w; and 1 960vw cm^{-1}. *m/e* (*I*): 259 (30); 231 (s); 203 (3); 175 (6); 147 (58); 119 (100); 91 (3); 78 (29); 41 (11); and 39 (17).

$[(CO)_5Cr\{C(O^-NMe_4^+)C_3H_5\}]$ *with tetrafluoroboric acid*. The salt (0·68 g, 2·0 mmol) was dissolved in water and then covered by a layer of hexane. The mixture was cooled to ice temperature and a few drops of a 50% solution of HBF_4 added to the vigorously stirred solution in the dark. A deep yellow colour was immediately visible in the aqueous layer and this passed rapidly into the organic phase. The organic layer was removed and dried ($CaSO_4$) in the dark. Crystallisation of the hexane solution at −20 °C gave *pentacarbonyl[cyclopropyl(hydroxy)carbene]chromium* as yellow needles (0·26 g, 50%), m.p. 64—66 °C (decomp.). $\nu_{max.}$: (CS_2) 3 495 (OH); 3 093vw; 3 002w; 1 030m (C_3H_5); (hexane) 2 067w; 1 967m; and 1 950s cm^{-1}. *m/e* (*I*): 262 (58); 234 (8); 206 (18); 178 (20); 150 (50); 122 (100); 91 (2); 41 (13); and 39 (13). The crystalline solid was extremely sensitive to light and also to heat.

$[(CO)_5Cr\{C(O^-NMe_4^+)CH_2SiMe_3\}]$ *with acetyl chloride and hydrogen azide*. Acetyl chloride (0·16 g, 2·0 mmol) was added to a solution of the salt (0·76 g, 2·0 mmol) in methylene chloride in the dark at room temperature. An ice-cold solution of hydrogen azide in benzene[34] (3·6 cm^3, 0·56N; 2·0 mmol) was added immediately to the brown solution. The mixture was stirred at ice temperature for 0·5 h after which a yellow solution was produced. Solvents were removed under reduced pressure and the residue was extracted with hexane. Crystallisation of the solution at −20 °C produced a solid (0·28 g, 60%) which was shown to be $[(C_2H_3N)Cr(CO)_5]$ by mass spectrometry [*m/e*: 233 (M^+); 205; 177; 149; 121; and 93] and to be a mixture of the isomers $[(MeCN)Cr(CO)_5]$ and $[(MeNC)Cr(CO)_5]$ by i.r. [$\nu_{max.}$ (hexane): 2 280w (–CN); 2 173w (–NC); 2 077m; 2 064m; 1 959vs; 1 953s; and 1 928m cm^{-1}] and n.m.r. [δ($CDCl_3$) 3·44 (CH_3NC) and 2·18 (CH_3CN) p.p.m.] spectroscopy. Comparison of the peak areas in the n.m.r. spectrum of the total sample showed that the ratio $[(MeNC)Cr(CO)_5]$: $[(MeCN)Cr(CO)_5]$ was *ca.* 4 : 1. The two isomeric complexes could not be separated by crystallisation, sublimation, or chromatography.

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$[(\mathrm{MeCONC})\mathrm{Cr(CO)_5}]$ *with methanol.* Methanol (2 $\mathrm{cm^3}$, in excess) was added to a stirred solution of $[(\mathrm{MeCONC})\mathrm{Cr(CO)_5}]$ (0·18 g, 0·69 mmol) in hexane at room temperature. Progress of the reaction was monitored by i.r. spectroscopy and was found to be complete after 1·5 h. The metal-containing product was identified as $[(\mathrm{HNC})\mathrm{Cr(CO)_5}]$. $\nu_{\mathrm{max.}}$ (hexane): 2 111vw; 2 069w; 1 956vs; and 1 926w,sh (lit.:[32] 2 115vw; 2 066w; 1 968s; and 1 934w,sh $\mathrm{cm^{-1}}$).

$[(\mathrm{Me_3CNC})\mathrm{Cr(CO)_5}]$ *with n-butyl-lithium.* A solution of n-butyl-lithium in hexane (1·8 $\mathrm{cm^3}$, 1·5M; 2·70 mmol) was added slowly to a light petroleum solution of $[(\mathrm{Me_3CNC})\mathrm{Cr(CO)_5}]$ (0·69 g, 2·50 mmol) at room temperature. The mixture was stirred for 4 h after which the solvent was removed under reduced pressure. The residue was dissolved in methylene chloride and treated with $\mathrm{Et_3OBF_4}$ (0·51 g, 2·70 mmol) in the same solvent. The pale yellow solution turned deep red immediately. The solvent was removed under reduced pressure and the residue was extracted with hexane. Three crystallisations of the hexane extracts at −20 °C gave unreacted $[(\mathrm{Me_3CNC})\mathrm{Cr(CO)_5}]$ (0·15 g, 22%). Elaboration of the mother liquor by chromatography (silica gel) gave a red *oil* which was identified as cis-*n-butyl-(ethoxy)carbene(t-butyl isocyano)tetracarbonylchromium* {0·61 g, 87% based on $[(\mathrm{Me_3CNC})\mathrm{Cr(CO)_5}]$ consumed}. $\nu_{\mathrm{max.}}$ (hexane): 2 121w (−N≡C); 2 011m; 1 940m; and 1 920s (−C≡O) $\mathrm{cm^{-1}}$. $\lambda_{\mathrm{max.}}$/nm (log ε) 245 (4·20) and 391 (3·38). $\delta(\mathrm{CDCl_3})$: 0·92 [3H, t, $-(\mathrm{CH_2})_3\mathrm{C}H_3$]; 1·48 [16H, m, $-\mathrm{CH_2C}H_2\mathrm{C}H_2\mathrm{Me}$, $-\mathrm{OCH_2C}H_3$; s, $(\mathrm{C}H_3)_3\mathrm{C}$]; 3·26 [2H, t, C(carbene)$-\mathrm{C}H_2-$]; and 5·12 (2H, q, $-\mathrm{OC}H_2-$) p.p.m. *m/e* (*I*): 361 (20, M^+); 333 (4); 305 (6); 277 (19); 249 (129); 220 (27); 192 (39); 166 (27); and 145 (100).

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