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CHEMISTRY OF [(TRIMETHYLSILYL)METHYL]CARBENE COMPLEXES OF CHROMIUM. THERMOLYSIS OF OXIDO–CARBENE SALTS

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SUMMARY

The synthesis and characterisation of the compounds $(CO)_5CrC(X)CH_2SiMe_3$ [$X=O^-NR_4^+$ (R=Me, Et) and OEt] is reported. The ethoxy–carbene complex is highly susceptible to nucleophilic attack (water, alcohols, NH_3) leading to rupture of the $Si–CH_2$ bond, but is not affected by HCl. The oxido–carbene complex reacts with acetyl chloride in CH_2Cl_2 and in MeCN to give $Me_4N[(CO)_5CrCl]$ and $(CO)_5CrNCMe$ respectively as a consequence of rupture of the Cr–C(carbene) bond. The formation of $[Cr(CO)_5]$ as an intermediate in these reactions is proposed. With iodine the oxido–carbene gives $Me_4N[(CO)_5CrI]$. Thermolysis of the oxido–carbene salts $(CO)_5CrC(ONMe_4)Y$ ($Y=CH_2SiMe_3$, 2-thienyl, cyclopropyl) results in fission of the Y–C(carbene) bond in each case. When Y is CH_2SiMe_3, or cyclopropyl the solid product of the reaction is a zwitterion carbene complex, $(CO)_5CrC(O^-)CH_2NMe_3^+$. The mechanism of these reactions is discussed. No product could be isolated from the reaction between $Cr(CO)_6$ and the ylide, Me_3NCH_2.

INTRODUCTION

The electronic effects of $(Me_3Si)_xCH_{3-x}$ groups are of considerable interest in relation to the concept of vertical stabilisation of cationic centres by neighbouring carbon–silicon bonds[1]. We have shown that the carbene carbon atom bound to the metal atom M in compounds of the type $(CO)_5MC(X)Y$ is best represented as a metal-stabilised carbocation[2] and that whereas the group X is required to be a π-donor, such as OR, SR or NR_2, the same is not necessarily required of the group Y[3]. The unusual conjugative electron releasing properties of $Y=Me_3SiCH_2$ relative to Y=Me could be expected to provide additional stabilisation of the carbocation in such complexes[4].

Many β-functional organosilicon compounds in which the β-function is acidic, as in Me_3SiCH_2COR, are particularly susceptible to cleavage of the $Si–CH_2$ bond by both acid[5] and base[6]. Having regard to the strong acceptor character of the $(CO)_5CrC(X)$ group[7], it was to be expected that the complexes $(CO)_5CrC(X)CH_2SiMe_3$ would contain $Si–CH_2$ bonds of enhanced reactivity towards nucleophiles and possibly also towards electrophiles.

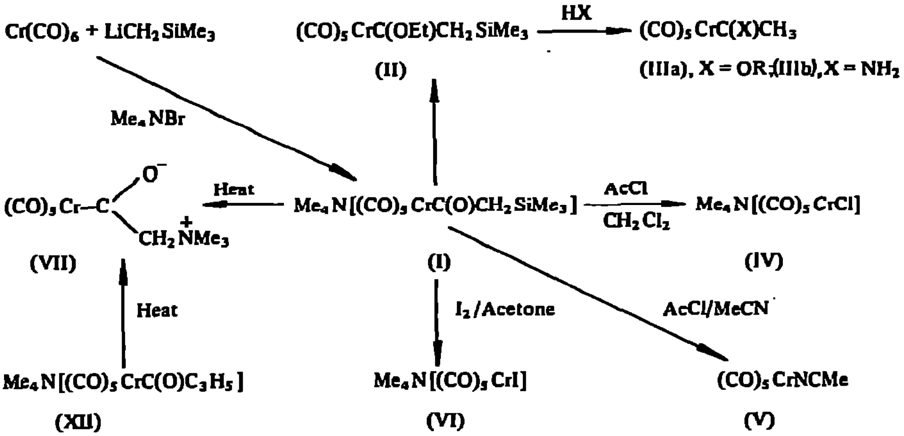
Finally, it is known that α-ketosilanes rearrange easily under a variety of conditions[8] to give compounds containing an Si–O bond. It might therefore be expected that the salt $Me_4N[(CO)_5CrC(O)CH_2SiMe_3]$ would undergo a thermal rearrangement with migration of the Me_3Si group from carbon to the negatively charged oxygen.

The extent to which these various expectations were fulfilled is described in the following account which also describes our work on the thermal decomposition of some other oxido–carbene salts, $Me_4N[(CO)_5CrC(O)Y]$ (Y = 2-thienyl, cyclopropyl).

RESULTS AND DISCUSSION

The reactions discussed below are outlined in Scheme 1 and in eqns. (1) and (2). The physical properties of the complexes prepared are recorded in the Experimental section. The number of carbene complexes containing the Me_3SiCH_2 group which we have been able to prepare has been severely restricted by the sensitivity of the $Si–CH_2$ bond in such compounds towards nucleophilic attack. The two compounds, $(CO)_5CrC(X)CH_2SiMe_3$ [(I), X = $ONMe_4$; (II), X = OEt] were prepared by standard methods[9].

SCHEME 1



Evidence in favour of the expected donor properties of the (trimethylsilyl)methyl group is provided by spectroscopic methods. In particular the proton NMR spectra of the two compounds show, from the position of the $Si–CH_2$ resonance and comparison with data on a number of other (trimethylsilyl)methyl compounds[10], that the $(CO)_5CrC(X)$ group is a strong acceptor in agreement with earlier studies. The mass spectrum of (II) shows that the $Si–CH_2$ bond is broken by electron impact with subsequent formation of $(CO)_5CrC(OEt)Me$ in the spectrometer source. The same spectrum also provides evidence for the transfer of the Me_3Si group from carbon to the ethoxy oxygen atom and formation of Me_3SiOEt in the spectrometer. The conclusions to be drawn from changes in the stretching frequency of the carbonyl group *trans* to the ligand, L, in $LM(CO)_5$ as indicated by $\nu(CO)A'_1$ must be treated with due caution but they suggest that, compared with $(CO)_5CrC(OEt)Me$, (ν 1962 cm^{-1})[11], the Me_3SiCH_2 group in (II) (1939 cm^{-1}) provides additional stabilisation of the carbocation.

Reactions involving cleavage of the Si–CH_2 bond

It is possible to prepare the ethoxy carbene complex (II) by the usual methods but the compound decomposes slowly in hexane solution to give $(CO)_5CrC(OEt)Me$ (IIIa)[11]. The reaction is apparently instantaneous when either water or methanol are added to compound (II). The addition of ammonia to an ice-cold solution of (II) affords $(CO)_5CrC(NH_2)Me$ (IIIb)[12] immediately. These reactions confirm the strong electrophilic character of the $(CO)_5CrC(OEt)$ group indicated by NMR spectroscopy. Compound (II) did not react with gaseous HCl and this is consistent both with the weak nucleophilic character of the chloride ion and the absence of a path by which (II) can be protonated, in contrast to β-ketosilanes[5].

Reactions involving cleavage of the Cr–C(carbene) bond

In contrast to other carbene salts[3], the salt (I) did not give a stable acetoxy–carbene complex when treated with acetyl chloride in methylene chloride solution. Instead, the only product isolated (89%) from the reaction was $Me_4N[(CO)_5CrCl]$ (IV)[13]. The carbene ligand $[Me_3SiCH_2(AcO)C:]$ must be presumed to have reacted further. There was no gaseous product of the reaction such as methane or CO and we were able to show that Me_4Si was not formed. The NMR spectrum of the reaction mixture after removal of (IV) showed signals which were consistent with the presence of Me_3SiCH_2 and acetyl groups; the mass spectrum was inconclusive, so that we are unable to identify the organic product(s) further.

The formation of (IV) in the manner described provides evidence for the formation of the pseudoradical species $[Cr(CO)_5]$ as an intermediate[14]. Further evidence in favour of this was obtained when the reaction between (I) and acetyl chloride was carried out in acetonitrile solution. In this case the solvent is a stronger donor than the chloride ion and the product of the reaction (82%) is the acetonitrile complex $(CO)_5CrNCMe$ (V)[15]. We were unable to identify the fate of the carbene ligand which could not be trapped with triethylsilane[16] to give $Et_3SiCH(OAc)CH_2SiMe_3$.

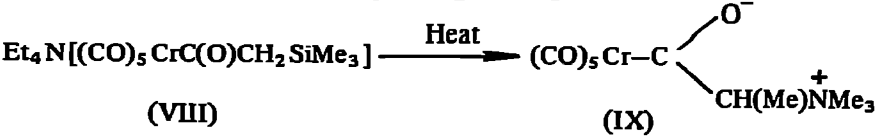
When the salt (I) is treated with iodine in acetone the product is $Me_4N[(CO)_5CrI]$(VI)[13]. It is reasonable to suggest that electrophilic substitution leads to the complex $(CO)_5CrC(OI)CH_2SiMe_3$ which is formally comparable to an acyl hypoiodite[17]. This intermediate is expected to undergo displacement of the carbene ligand by iodine ion very easily. Once again we have been unable to determine the fate of the ligand, $[Me_3SiCH_2–C–OI]$, in this reaction.

Reactions involving cleavage of C(carbene)–C bonds: thermolysis of carbene salts

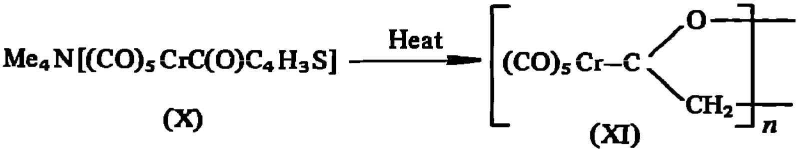
As outlined earlier, previous experience[8] would lead to the expectation that thermal decomposition of (I) would give $Me_4N[(CO)_5CrC(OSiMe_3)CH_2]$ as a result of transfer of the organosilicon group from carbon to oxygen. However, when (I) was heated at 110–120° and 0.1 mmHg for 3 h the products were identified as tetramethylsilane and a zwitterionic carbene complex, $(CO)_5CrC(O^-)CH_2N^+Me_3$(VII). The latter was identified by its molecular weight, analysis and infrared and electronic spectra. Compound (VII) is hygroscopic, insoluble in non-polar solvents, slightly soluble in acetone and moderately soluble in polar solvents such as acetonitrile and dimethyl sulphoxide, all of which is consistent with the zwitterion character; the compound may be considered as a formal analogue of betaine, $Me_3N^+CH_2COO^-$.

In an attempt to prepare (VII) directly we have carried out the reaction between $Cr(CO)_6$ and the ylide, Me_3NCH_2[18], in tetrahydrofuran solution at room temperature in the dark. A brown precipitate formed immediately which, however, decomposed during a few minutes to give an insoluble white solid and a yellow solution which was shown to contain $Cr(CO)_6$ only. No evidence for the formation of (VII) was obtained from these experiments. It may be that (VII) is produced (brown precipitate) but decomposes in the presence of excess strong base and polar solvent.

In order to obtain more information about the mechanism of the formation of (VII), we have prepared $Et_4N[(CO)_5CrC(O)CH_2SiMe_3]$, (VIII), and studied its thermal decomposition. The products of the thermal decomposition of the tetraethylammonium salt, (VIII), were Me_4Si and the zwitterionic carbene compound $(CO)_5CrC(O^-)CHMeN^+Et_3$ (IX). Traces of triethylamine were also produced consistent with the known sensitivity of tetraethylammonium salts to thermal decomposition. Taken together these results indicate that the mechanism of thermolysis involves C(carbene)–CH_2 bond rupture followed by proton abstraction from the NR_4^+ (R = Me, Et) group to give Me_4Si in each case. The presumed products at this stage, $Cr(CO)_6$ and $R'C^-HN^+(CH_2R')_3$ (R = H, Me) can then react to give (VII) and (IX) respectively. The alternative free radical mechanism involving Si–CH_2 bond rupture would have produced Me_3SiEt as the silicon-containing product from the thermolysis of (VIII). If, indeed, the ylide mechanism operates, it shows that the C(carbene)–CH_2 bond of (I) and of (VIII) is broken on thermolysis rather than the Si–CH_2 bond as found in other Me_3SiCH_2X compounds[8].



(VIII) (IX) (1)



(X) (XI) (2)

To test the generality of this conclusion we have examined the thermolysis of $Me_4N[(CO)_5CrC(O)C_4H_3S]$, (X)[19], under conditions similar to those used for the thermolysis(I) and (VIII). The formation of thiophen showed that C(carbene)–C bond fission had occurred. In addition to thiophen, a quantity of trimethylamine was obtained. The solid residue could not be characterised completely because of inconsistent analyses. On the basis of the evidence available we suggest that the solid product is either dimeric or polymeric, $[(CO)_5CrC(O)CH_2]_n$ ($n \geqslant 2$) (XI). Attempts to determine the molecular weight of (XI) by osmometry and by Rast's method were unsuccessful because of decomposition and insolubility problems respectively. It is reasonable to suggest that (XI) is formed by way of the zwitterion (VII) which then decomposes further under the influence of thiophen (a proton acceptor). This is analogous to the Hoffmann degradation of β-amino alcohols[20]. We have attempted to test this hypothesis by heating (VII) with pure thiophen in an evacuated sealed tube but no reaction was observed.

Further evidence of the influence of the group Y in the salts $Me_4N[(CO)_5CrC(O)Y]$ upon the nature of the thermal decomposition product was obtained when the cyclopropyl salt ($Y=C_3H_5$) was heated under the usual conditions. This gave cyclopropane as a result of C(carbene)–C_3H_5 bond rupture together with traces of trimethylamine as the only volatile organic products. The solid residue was shown to be the zwitterionic carbene compound, (VII). There was no evidence of thermolytic ring opening of the cyclopropane ring.

CONCLUSIONS

The introduction of a (trimethylsilyl)methyl group as a substituent at the carbene carbon in metal-stabilised carbocation systems results in enhanced reactivity of the Si–CH_2 bond towards nucleophiles as a consequence of the strong electron withdrawing power of the $(CO)_5CrC(X)$ group. This is also reflected in the spectroscopic properties of the compounds.

We have shown that electrophilic attack by Q–Z(Q=MeCO, I; Z=Cl, I) on the salt (I) results in complete displacement of the carbene ligand [Me_3SiCH_2–C–OQ] and the formation of $[(CO)_5CrZ]^-$ *via* the intermediate $[Cr(CO)_5]$. This reaction is in marked contrast to the effect of heat upon the salt (I) which causes the C(carbene)–C bond to break. This thermolytic behaviour, which appears to be general for compounds of the type $R_4N[(CO)_5CrC(O)Y]$ differs from that of both alkoxy- and amino-carbene complexes which have been investigated[21] and which suffer rupture of the metal–C(carbene) bond in each case.

In this way, we have established that, under appropriate conditions, it is possible to cause rupture of each of the bonds to carbon in the fragment [MC(X)Y] of transition metal carbene complexes in a specific and differential manner.

EXPERIMENTAL

(Chloromethyl)trimethylsilane was purchased from P.C.R. Chemicals, Gainsville, Florida. Chromium hexacarbonyl was purchased from Strem Chemicals Inc. Andover, Mass. n-Butyllithium was purchased from Honeywell and Stein Ltd., London, and estimated by the double titration method[22]. $Et_3O^+BF_4^-$[23] and Me_3SiCH_2Li[24] were prepared by standard methods. Me_3SiCH_2Li was estimated by single titration with 0.1 *N* hydrochloric acid. Cyclopropyl bromide was purchased from Fluka AG. General features of the methods used are the same as in previous work from this laboratory[3].

Preparation of $(CO)_5CrC(O^-N^+Me_4)CH_2SiMe_3$ *(I)*

A solution of Me_3SiCH_2Li (110 ml of 0.3 *N*; 33.0 mmol) in ether was added over 2 h to a rapidly stirred solution of chromium hexacarbonyl (7.2 g, 33.0 mmol) in ether (500 ml) and the mixture was stirred at room temperature for a further 2 h. The ether solvent was removed under reduced pressure and then water was added to dissolve the lithium salt. A saturated solution of tetramethylammonium bromide (8.0 g, 51.6 mmol) in water (10 ml) was added to this aqueous solution and a yellow precipitate was formed immediately. This was filtered, dried under reduced pressure and then dissolved in methylene chloride. Addition of pentane to the solution caused precipitation of the salt; this purification procedure was repeated twice further to give (I) (6.5 g; 17.0 mmol, 50%) as pale green crystals, M.p. 94–95°. (Found: C, 43.9; H, 6.3;

N, 3.6; Cr, 13.3. $C_{14}H_{23}CrNO_6Si$ calcd.: C, 44.1; H, 6.3; N, 3.7; Cr, 13.6%.) ν_{max} (CH_2Cl_2): 2031 w, 1929 w(sh), 1896 vs, 1879 m(sh) cm^{-1}. λ_{max}nm (log ε) (CH_2Cl_2): 241 (4.39), 332 (3.36). δ (acetone-d_6) 0.06 (Me_3Si), 2.75 (CH_2), 3.52 (N^+Me_4) ppm.

Preparation of $(CO)_5CrC(OEt)CH_2SiMe_3$ (II)

A solution of $Et_3O^+BF_4^-$ (0.90 g, 4.8 mmol; 10% excess) in methylene chloride was added to a stirred solution of (I) (1.63 g, 4.3 mmol) in the same solvent. The solvent was removed under reduced pressure and the residue extracted with hexane. The hexane solution was then passed through anhydrous sodium sulphate and filtered (G3). After removal of solvent under reduced pressure, (II) was obtained (65%) as an orange liquid, M.p. ca. 0° .(Found: C, 42.5; H, 4.4; Cr, 16.2. $C_{12}H_{16}CrO_6Si$ calcd.: C, 43.0; H, 4.8; Cr, 15.5%.) ν_{max}(hexane): 2065 m, 1990 w, 1950 vs, 1939 s cm^{-1}. λ_{max}nm (log ε) (hexane): ca. 250 (4.52), 373 (3.71). δ(CCl_4): 0.17 (Me_3Si), 1.64 (3 H, t, CH_3), 3.48 (2 H, s, CH_2Si), 4.98 (2 H, q, OCH_2); ($CDCl_3$): 0.19 (Me_3Si), 1.61 (3 H, t, CH_3), 3.50 (2 H, s, CH_2Si), 4.95 (2 H, q, OCH_2); (acetone-d_6): 0.17 (Me_3Si), 1.67 (3 H, t, CH_3), 3.60 (2 H, s, CH_2Si), 5.02 (2 H, q, OCH_2); (C_6D_6): 0.18 (Me_3Si), 1.28 (3H, t, CH_3), 3.42 (2 H, s, CH_2Si), 4.59 (2 H, q, OCH_2) ppm. m/e(*I*): 336 (3) M^+, 308 (5), 288 (1), 280 (5), 252 (2), 224 (13), 196 (100), 144 (7), 129 (10), 103 (66), 75 (52), 73 (68), 58 (6). Compound (II) decomposes slowly when stored under nitrogen at −10°. In n-hexane solution this decomposition can be monitored by IR spectroscopy by observing the appearance of bands due to $Cr(CO)_6$ (1990 cm^{-1}) and to $(CO)_5CrC(OEt)Me$[10] at 2065 w, 1981 w, 1963 m, 1950 vs cm^{-1}. The mass spectrum of (II) also provides evidence for the formation of $(CO)_5CrC(OEt)Me$ by the steady increase of major peaks at m/e 264, 236, 208, 180, 152 and 124 with lapse of time.

Reaction of (II) with ammonia

Ammonia (from evaporation of liquid ammonia) was passed through a stirred, ice-cooled, hexane solution of (II) (0.34 g, 1.0 mmol) until the solution had become a light yellow in colour. The solution was filtered and the solvent partially removed under reduced pressure so that crystallisation at −20° produced yellow crystals, (0.20 g, 85%) of $(CO)_5CrC(NH_2)Me$, M.p. 72–73°, ν_{max}(hexane): 2064 m, 1974 w, 1950 s, 1942 vs cm^{-1} (lit.[12] m.p. 76–77°; ν_{max}(hexane): 2063 m, 1964 w, 1949 s, 1941 vs cm^{-1}).

Reaction of (I) with acetyl chloride

Acetyl chloride (0.24 g, 3.1 mmol) was slowly added to a stirred solution of (I) (1.16 g, 3.1 mmol) in methylene chloride in the dark. A brown colouration was observed immediately and after a few minutes a yellow-orange precipitate was formed. The solvent was removed under reduced pressure. The residue was completely insoluble in hexane and was, therefore, extracted with methylene chloride. Precipitation from the methylene chloride solution with pentane gave $Me_4N[(CO)_5CrCl]$ (IV) (97%) as orange prisms[13], M.p. 270° (dec). (Found: C, 35.7; H, 3.8; N, 5.2. $C_9H_{12}ClCrNO_5$ calcd.: C, 35.7; H, 3.9; N, 4.9%.) ν_{max}(CH_2Cl_2): 2064 w, 1981 w, 1926 s, 1862 m cm^{-1}. λ_{max}nm (log ε) (CH_2Cl_2): 258 (4.20), 430 (3.26). Any gaseous products of the reaction were collected and examined by mass spectrometry which showed that neither methane nor carbon monoxide are formed. Filtration of the methylene chloride solution to remove the salt product and examination of the filtrate by NMR showed signals at δ 0.06, 0.16, 0.24 (Me_3SiCH_2 group) and 1.98 ($COCH_3$) ppm together with signals from the solvent and from (IV). This spectrum was shown to be distinct from one recorded on a 1/1 mixture of Me_4Si and CH_3COCl in the same solvent.

The reaction of (I) with acetyl chloride in acetonitrile solution

The complex (I) (0.38 g, 1.0 mmol), was dissolved in acetonitrile (30 ml) and acetyl chloride (0.08 g, 1.0 mmol) was slowly added. A brown colouration was immediately observed which quickly disappeared to give a yellow solution. After stirring for 10 min, the solvent was removed under reduced pressure and the residue was extracted with hexane/ether (2/1 v/v). Crystallisation of this solution at −20° produced yellow crystals of $(CO)_5CrNCMe$ (V), (0.19 g, 82%). M.p. 69–70°. ν_{max}(hexane): 2077 w, 1953 s, 1928 m cm^{-1} (lit. [15]m.p. 71°; ν_{max}(hexane)[25]: 2077 m, 1951 vs, 1927 cm^{-1}).

Reaction of (I) with iodine

Iodine (0.13 g, 1.02 mmol) was dissolved in acetone and the solution was added slowly during 30 min to a stirred solution of (I) (0.38 g, 1.0 mmol) in acetone. The colour changed to orange and finally to brown. The solvent and excess iodine were removed under reduced pressure. Extraction with methylene chloride and precipitation with pentane gave $Me_4N[(CO)_5CrI]$ (VI) (85%) as orange prisms[13], M.p. 270°(dec). (Found: C, 26.4; H, 3.4; N, 4.7; Cr, 12.2. $C_9H_{12}CrINO_5$ calcd.: C, 27.4; H, 3.1; N, 3.6; Cr, 13.2%.) $\nu_{max}(CH_2Cl_2)$: 2054 w, 1926 s, 1873 m cm^{-1}; λ_{max} nm (log ε) (CH_2Cl_2): 258 (4.20), 430 (3.26).

Thermolysis of (I)

Compound (I) (1.24 g, 3.3 mmol) was heated at 110–120° under vacuum (ca. 0.1 mmHg) for 3 h. Volatile material was collected by condensation in a liquid nitrogen-cooled vessel. The residue was shown to be a brown solid {[(trimethylammonio)methyl](oxido)carbene}pentacarbonylchromium (VII) (0.96 g) (Found: C, 40.9; H, 5.4; N, 4.3; Cr, 17.9. Mol. wt. 310. $C_{10}H_{11}CrNO_6$ calcd.: C, 41.0; H, 3.8; N, 4.8; Cr, 17.8%. Mol. wt. 293.) ν_{max}(MeCN): 2022 vw, 1944 m, 1887 vs (*E*) 1915 s(*A'*) cm^{-1}. λ_{max}nm (MeCN): ca. 260, 360. The compound is very hygroscopic, insoluble in non-polar solvents, slightly soluble in acetone and moderately soluble in acetonitrile and dimethylsulphoxide. NMR spectra of the volatile liquid product (0.28 g, mol. wt. 80) (CCl_4 solution) showed only one signal which increased in intensity on addition of pure tetramethylsilane (mol. wt. 88). The IR spectrum of the liquid product ($CHCl_3$ solution) was identical with that of an authentic sample of tetramethylsilane in the same solvent. The identification was confirmed by mass spectrometry.

$(CO)_5CrC(O^-NEt_4^+)CH_2SiMe_3$ *(VIII)*

Preparation of $(CO)_5CrC(O^-NEt_4^+)CH_2SiMe_3$ (VIII), followed the procedure outlined for (I) using Et_4NBr. The salt (VIII) was obtained (42%) as light green crystals. (Found: C, 47.3; H, 7.5; N, 3.9; Cr, 8.7. $C_{18}H_{31}CrNO_6Si$ calcd.: C, 49.4; H, 7.1; N, 3.2; Cr, 11.9%.) $\nu_{max}(CH_2Cl_2)$: 2029 w, 1930(sh), 1893 s, 1873 m(sh).

Thermolysis of (VIII)

Thermolysis of (VIII) (0.39 g, 0.89 mmol) by the method described for (I) gave {[1-(triethylammonio)ethyl](oxido)carbene} pentacarbonylchromium (IX) as a brown solid (0.29 g, mol. wt. 325). (Found: C, 48.5; H, 6.0; N, 3.9; Cr, 15.0. Mol. wt. 325. $C_{14}H_{19}CrNO_6$ calcd.: C, 48.1; H, 5.4; N, 4.0; Cr, 14.9%. Mol. wt. 349. The liquid product (0.075 g, mol. wt. 85) was shown by NMR, IR and mass spectroscopy to consist of tetramethylsilane (95%; mol. wt. 88) with a trace of triethylamine.

Reaction of chromium hexacarbonyl with trimethylammonium ylide, $Me_3N^+C^-H_2$

A solution of n-butyllithium (22.2 ml of 1.5 *N*; 33.2 mmol) was added to a rapidly stirred suspension of tetramethylammonium bromide (2.55 g, 16.6 mmol) in ether at ice temperature. The mixture was allowed to warm to room temperature and then stirred for 40 h. The solvent was decanted and the residue washed with three 100 ml portions of ether in order to remove unreacted n-butyllithium, lithium bromide and any dimetalated product which had formed.

The residual white solid was dissolved in tetrahydrofuran (500 ml) and chromium hexacarbonyl (3.65 g, 16.6 mmol) was quickly added to the solution at room temperature in the dark. An immediate brown precipitate was formed which over a few minutes, decomposed to give a white solid which was insoluble in all the solvents tried and a yellow tetrahydrofuran solution, which was shown by IR spectroscopy to contain chromium hexacarbonyl (ν_{max} 1990 cm^{-1}) as the only tetrahydrofuran-soluble metal carbonyl component.

Thermolysis of $(CO)_5Cr(O^-NMe_4^+)C_4H_3S$ (X)

The salt (X)[19] (1.85 g, 4.9 mmol) was heated at 110–120° under vacuum (ca. 0.1 mmHg) for 4 h. All volatile products were collected by condensation in a liquid nitrogen-cooled vessel. The liquid products (0.30 g) were characterised by NMR, and mass spectroscopy and shown to consist of thiophen and trimethylamine. The solid residue (1.14 g) obtained as brown plates, was insoluble in hydrocarbon solvents, in chloroform and in water, fairly soluble in acetone and soluble in acetonitrile and in dimethyl sulphoxide. (Found: C, 34.2; H, 4.5; N, 3.9; Cr 20.0. Mol. wt. 232 *n* $(C_7H_2CrO_6)_n$ calcd.: C, 35.9; H, 0.9; Cr, 22.2%. Mol. wt. 234·*n*.) ν_{max}(MeCN): 2040 w, 1916 vs (*E*), 1958 s (A'_1) cm^{-1}. λ_{max}(MeCN): 260, 331 nm.

Preparation of $(CO)_5CrC(O^-NMe_4^+)C_3H_5$ (XII)

An ether solution of cyclopropyllithium[26] (126 ml of 0.46 *N* solution; 57.9 mmol) was added over 2 h to a stirred mixture of chromium hexacarbonyl (12.7 g, 57.9 mmol) in ether at room temperature. The mixture was allowed to stir for a further 2 h at room temperature. Subsequent elaboration followed the procedure outlined for (I) and gave (XII) as a yellow powder (10.5 g, 54%). M.p. 123–125°. (Found: C, 46.4; H, 5.3; N, 4.5; Cr, 15.4. $C_{13}H_{17}CrNO_6$ calcd.: C, 46.6; H, 5.1; N, 4.2; Cr, 15.5%.) ν_{max}(CH_2Cl_2): 2032 w, 1932 w, 1879 s(*E*), 1880 m(sh) (A'_1) cm^{-1}, λ_{max} nm (log ε) (CH_2Cl_2): 249 (4.21), 344 (3.20). δ(acetone-d_6): 0.31 (2 H, m, H2, H4), 0.65 (2 H, m, H3, H5), 2.79 (1 H, m, H1), 3.44 (12 H, s, NMe_4) ppm.

Thermolysis of $(CO)_5CrC(O^-NMe_4^+)C_3H_5$ (XII)

The salt (XII) (0.73 g, 2.2 mmol) was heated at 110–120° under vacuum (ca.

0.1 mmHg) for 4 h. All volatile products were collected by condensation in a liquid nitrogen-cooled vessel. The brown solid residue (0.26 g) was shown to be identical with compound (VII) by microanalysis and IR spectroscopy. The condensate, which was gaseous at room temperature, was characterised by NMR spectroscopy. In $CDCl_3$ solution at $-40°$ the spectrum showed two singlets at δ 0.22 and 2.21 ppm. The former (major) signal is due to cyclopropane [lit.[27] $\delta(C_3H_6)$ 0.20 ppm] and the latter (minor) signal is due to trimethylamine [lit.[28] $\delta(NCH_3)$ 2.30 ppm]. The molecular weight of the condensate was estimated to be 48 (C_3H_6, mol. wt. 42; NMe_3, mol. wt. 59).

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