A Novel Carbon Dioxide Complex: Synthesis and Crystal Structure of $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$†

By Garry S. Bristow, Peter B. Hitchcock, and Michael F. Lappert
(*School of Chemistry and Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary Reduction of $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)Cl]$ with sodium amalgam in tetrahydrofuran under one atmosphere of carbon dioxide yields $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$ (**1**), a moderately air-stable, thermally robust complex; the *X*-ray structure determination of complex (**1**) shows the distances Nb–CO_2, Nb–OCO, C–ONb, and C=O to be 2·144(7), 2·173(4), 1·283(8), and 1·216(8) Å, respectively, and ∠O–C–O 132·4(7)°.

Attention has recently been drawn to intensive efforts during the past decade to prepare and characterise metal-bound CO_2-complexes, especially in the context of CO_2 activation.[1] Numerous difficulties have been encountered, including the formation (and misassignment, often on the basis of i.r. data, as CO_2-adducts) of hydrogen carbonato–, carbonato–, and carboxylato–metal complexes. Only two CO_2–metal (mononuclear) complexes have previously been structurally verified, the d^{10} complex $[Ni\{P(cyclohexyl)_3\}_2(\eta^2\text{-}CO_2)]$[2] and the d^8 complex $[\{Co(pr\text{-}salen)K(\mu\text{-}CO_2)(thf)\}_n]$ (pr-salenH_2 = *o*–HO-C_6H_4.C(Pr^n)=N$[CH_2]_2$N=C(Pr^n)·C_6H_4·OH-*o*; thf = tetrahydrofuran);[3] in the latter complex the CO_2 is *C*-bonded to Co^I and *O,O′*-bound to K^+, which is tetrahedrally co-ordinated to two CO_2 molecules of adjacent Co^I units.

$[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)L]$
(**1**) L = η^2-CO_2
(**2**) L = CO
(**3**) L = CO_3

We now report the synthesis and *X*-ray structure of the d^2 18-electron compound $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$ (**1**), which is of interest because (i) it is the first authentic CO_2-complex of an early d-block metal, and of a hard oxophilic transition element; (ii) the CO_2 ligand lies in close proximity to an alkyl group, but does not insert into the M–R bond; (iii) of its thermal stability (and thus none of the decomposition pathways reported[4] for labile CO_2–metal adducts is readily accessible); (iv) it represents a remarkably stable alkylniobium complex; and (v) it is obtained under ambient conditions in a rapid reaction.

Complex (**1**) was prepared by the addition of $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)Cl]$[5] to a freeze-degassed suspension of excess of Na–Hg (0·6% w/w) in thf under CO_2 (1 atm). Vigorous shaking caused the mixture to change from green to brown in *ca.* 30 s. Stirring for a further ½ h, filtration, removal of solvent, extraction with toluene, and cooling produced fine white needles of the title compound (**1**) (34%), m.p. 131 °C; δ ($^{13}CO_2$) −200·5 p.p.m. ($CDCl_3$); ν(CO) 1695 cm^{-1} (Nujol); it showed appropriate microanalytical and other i.r. and ^1H and ^{13}C n.m.r. features. Single crystals of complex (**1**) were obtained from CH_2Cl_2–n-C_5H_{12}.

It appears that $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(CO)]$ (**2**) and $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(CO_3)]$ (**3**) are also produced in the above reaction. Complex (**2**) was isolated when the reaction mixture was not shaken but stirred slowly for *ca.* 12 h prior to work-up. The presence of a small amount of complex (**3**) was inferred from the very weak e.s.r. signal attributed to a niobium-centred radical obtained upon $Na[C_{10}H_8]$–thf re-

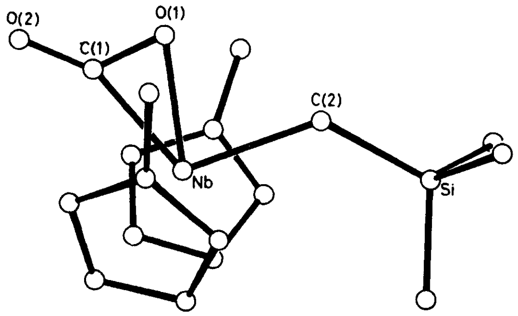

Figure. The molecular structure of $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$ (**1**). Relevant dimensions are Nb–C(1) 2·144(7), Nb–O(1) 2·173(4), C(1)–O(1) 1·283(8), and C(1)–O(2) 1·216(8) Å; O(1)–C(1)–O(2) 132·4(7)°.

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† No reprints available.

duction of impure (crystallised once only) complex (**2**); pure (**1**) gave a diamagnetic product under these conditions. The same signal [g_{av} 2·032 and $a(^{93}Nb)$ 9·31 mT in thf at *ca.* 20 °C] was also obtained from the reaction product of $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)Cl]$, Na–Hg, and Na_2CO_3 in thf.

The molecular structure of complex (**1**) (see Figure) indicates why it is stable. The orientation of the CO_2 ligand is such that insertion into the metal–alkyl bond would produce not the carboxylato-complex but a metallocarboxylate ester $L_nNb\text{–}CO_2R$; this type of product has been claimed only once,[4] and its formation is in any case less favoured than that of the isomeric $L_nNbOCOR$. Moreover, complex (**1**) is a co-ordinatively saturated 18-electron species to which the CO_2 ligand is firmly bound.

Crystal data for complex (**1**): $C_{17}H_{25}NbO_2Si$, monoclinic, space group $P2_1/c$, $a = 16{\cdot}647(9)$, $b = 7{\cdot}005(2)$, $c = 15{\cdot}468(7)$ Å, $\beta = 91{\cdot}43(4)°$, $Z = 4$. The structure has been refined to $R = 0{\cdot}064$ for 2127 reflections with $I > \sigma(I)$, measured on an Enraf-Nonius CAD-4 diffractometer.‡

The bonding of the CO_2 ligand to the Nb *via* one C=O bond is similar to that[2] in $[Ni\{P(cyclohexyl)_3\}_2(\eta^2\text{-}CO_2)]$ rather than the *C*-bonded mode seen in the cobalt complex $[\{Co(pr\text{-}salen)K(\mu\text{-}CO_2)(thf)\}_n]$.[3] However, both the co-ordinated C=O (1·283 Å) and the non-co-ordinated C=O (1·216 Å) bonds seem to be longer than in the Ni complex, and are more in agreement with the effects seen in the diphenylketen complex $[V(\eta\text{-}C_5H_5)_2(\eta^2\text{-}OCCPh_2)]$,[6] where the co-ordinated C=O is 1·290(6) Å and the non-co-ordinated C=C is significantly lengthened from that in the free ligand. In the Nb complex the O–C–O angle of 132·4° is essentially the same as that in the Ni complex.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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