ORGANOMETALLICS

Volume 13, Number 8, August 1994

Communications

$[(C_3{}^tBu_3)V(CO)_4]$: Partial Insertion of Vanadium into the Cyclopropenyl Ring

Ralph B. Blunden, F. Geoffrey N. Cloke,* Peter B. Hitchcock, and Peter Scott*

School of Chemistry and Molecular Sciences, University of Sussex,
Falmer, Brighton BN1 9QJ, U.K.

Received April 11, 1994®

Summary: Photolysis of a mixture of tri-tert-butylcyclopropenium tetrafluoroborate and sodium hexacarbonylvanadate gives the title complex, the molecular structure of which shows it to be the first example of partial insertion of an early-transition-metal atom into the cyclopropenyl ring. Variable-temperature ^{13}C *NMR data are consistent with there being an appreciable amount of* σ*-character in the ring–metal bond. These observations are rationalized with reference to a molecular orbital description of the ligand–metal bonding interaction. The compound* ($C_{19}H_{27}VO_4$) *crystallizes in the monoclinic space group* $P2_1/n$, *with* $a = 8.525(2)$ Å, $b = 26.637(8)$ Å, $c = 8.920(2)$ Å, $\beta = 103.42(2)°$, *and* $Z = 4$.

The chemistry of η-cyclopropenyl complexes of the transition metals is receiving renewed attention. In particular, Hughes and co-workers have made extensive investigations into the structural and bonding characteristics of η^3-cyclopropenyl complexes of the middle and later transition metals.[1] To date, however, no such complexes of group 3 or 4 metals are known, and only one of group 5 has been isolated.[2] Also, cyclopropenyl complexes and the isomeric metallacyclobutadiene structures have been implicated as intermediates in alkene metathesis reactions,[3] and the conversion between these two structures (Figure 1) has been investigated by Hoffman.[4]

We have recently synthesized the complex $[(C_3{}^tBu_3)V(CO)_4]$ (**1**), which we have found to be first early-transition-metal complex with the intermediate structure ii.[5] We report here its characterization by variable-temperature NMR and X-ray crystallographic studies, as well as a rationalization of the arrested insertion of the metal atom into the ring.

Photolysis of a 1:1 mixture of sodium hexacarbonylvanadate and tri-*tert*-butylcyclopropenium tetrafluoroborate in tetrahydrofuran leads to the formation of a blue-green solution from which deep blue crystals of the title complex **1** can be isolated in *ca.* 50% yield after crystallization from petroleum ether.[6] **1** is only moderately air-sensitive and can be chromatographed on basic alumina under an atmosphere of argon. It sublimes at room temperature onto a liquid-nitrogen-cooled probe.

Single crystals of **1** (grown by slow cooling of a pentane solution to −50 °C) were isolated directly from the mother liquor without drying and subjected to an

---

® Abstract published in *Advance ACS Abstracts,* June 15, 1994.

[1] (a) Lichtenberger, D. L.; Hoppe, M. L.; Subramanian, L.; Kober, E. M.; Hughes, R. P.; Hubbard, J. L.; Tucker, D. S. *Organometallics* **1993**, *12*, 2025. (b) Ditchfield, R.; Hughes, R. P.; Tucker, D. S.; Bierwagen, E. P.; Robbins, J.; Robinson, D. J.; Zakutansky, J. A. *Organometallics* **1993**, *12*, 2258. (c) Hughes, R. P.; Tucker, D. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3069. (d) Hughes, R. P.; Tucker, D. S. *Organometallics* **1993**, *12*, 4736. (e) Shen, J. K.; Tucker, D. S.; Basolo, F.; Hughes, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 11312.

[2] Reaction of $[C_3Ph_3]PF_6$ with $Na[V(CO)_6]$ under photolysis gives a material formulated as $[(\eta^3\text{-}C_3Ph_3)V(CO)_5]$ on the basis of spectroscopic evidence: Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 345.

[3] Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

[4] Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570.

[5] McLure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1973**, *54*, C59. The complex $[Pt(C_3Ph_3)(PPh_3)_2][PF_6]$ reported in this paper also contains what appears to be an η^2-cyclopropenyl ring.

0276-7333/94/2313-2917$04.50/0

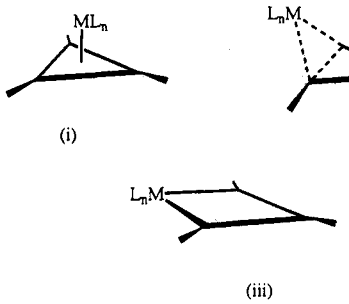


Figure 1. Reaction coordinate from (i) η^3-cyclopropenyl through (ii) an intermediate structure to (iii) metallacyclobutadiene.

X-ray structural analysis.[7] The molecular structure is shown in Figure 2 and a view perpendicular to the C_3 plane in Figure 3.

The most striking feature of the structure is that the V atom is not symmetrically bonded to the ring but lies much closer to one edge of the triangle. The angle ϕ (Figure 4) between the plane of the ring and that defined by V, C(6), and C(7) of 106.86° compares with 111° in $[Pt(C_3Ph_3)(PPh_3)_2][PF_6]$,[5] the only other known structure of this type. The distance C(6)—C(7) of 1.710(11) Å is, however, somewhat longer than the corresponding distance of 1.58(2) Å in $[Pt(C_3Ph_3)(PPh_3)_2][PF_6]$ and 1.50 Å in the cyclopropene complex $[Pt(PPh_3)_2(C_3H_2Me_2)]$.[8] Since the usual C—C distance in cyclopropanes is *ca.* 1.5 Å,[9] we must conclude that the bond between C(6) and C(7) is rather weak.

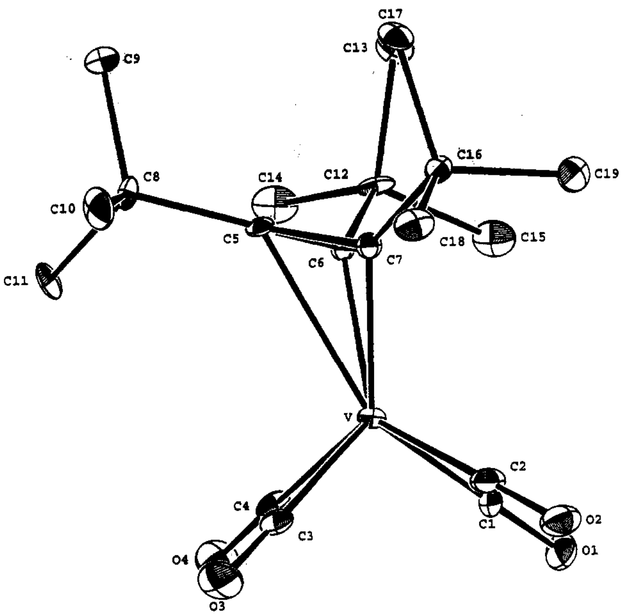


Figure 2. ORTEP[16] drawing of the molecular structure of **1** with thermal ellipsoids at the 20% level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): V—C(1), 1.932(9); V—C(2), 1.918(9); V—C(3), 1.965(9); V—C(4), 1.958(7); V—C(5), 2.416(9); V—C(6), 2.056(9); V—C(7), 2.025(8); C(5)—C(6), 1.380(11); C(5)—C(7), 1.412(12); C(5)—C(8), 1.506(12); C(6)—C(7), 1.710(11); C(6)—C(12), 1.491(12); C(7)—C(16), 1.515(10); C(6)—V—C(7), 49.5(3); C(6)—C(5)—C(7), 75.5(6); C(5)—C(6)—C(7), 53.1(5); C(5)—C(7)—C(6), 51.4(5).

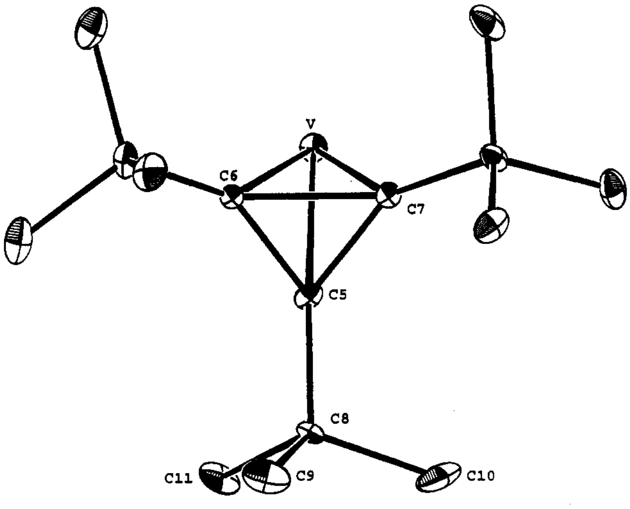


Figure 3. ORTEP[16] view of the molecular structure of **1** viewed perpendicular to the plane of the C_3 ring. Hydrogen atoms and carbonyl ligands are omitted for clarity.

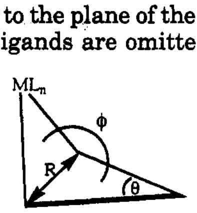


Figure 4. Parameters used in the discussion of the geometry of the cyclopropenylvanadium fragment of **1**.[4]

The atom C(5), which has planar geometry (sp^2) within esd's, is 2.416(9) Å from V and is thus not considered to be within bonding distance. The V—C(6) and V—C(7) bonds of 2.056(9) and 2.025(8) Å, respectively, compare well with those of 2.057(8) and 2.043(5) Å in the vanadium alkyl $Li[V(^tBu_3SiN)_2Me_2]$[10] and are rather shorter than those in compounds of lower formal oxidation states.[11] The atoms C(12) and C(16) lie some 0.80(1) and 0.91(1) Å, respectively, out of the plane

---

(6) Synthesis and data for **1**: A suspension of sodium hexacarbonylvanadate (0.50 g, 1.70 mmol) and tri-*tert*-butylcyclopropenium tetrafluoroborate (0.41 g, 1.70 mmol) in tetrahydrofuran (50 cm^3) was stirred for 30 min and then photolyzed for a further 2 h (using a medium-pressure mercury lamp) under a slow stream of argon. The resulting blue-green solution was evaporated to dryness, extracted into petroleum ether, and passed down a short column of alumina (5% w/w H_2O) before crystallizing at −50 °C and drying *in vacuo* (yield 0.51 g, 81%). ^1H NMR (250 MHz, $[^2H_6]$benzene, 293 K): δ 0.95 (CH_3). ^{13}C NMR ($[^2H_6]$benzene, 293 K): δ 37.4 [quat $C(CH_3)_3$], 31.3 [$C(CH_3)_3$]. ^{13}C NMR ($[^2H_8]$THF, 183 K): δ 158.3 (ring quat), 38.2 [quat $C(CH_3)_3$], 31.2 [$C(CH_3)_3$]. Anal. Calcd for $C_{19}H_{37}VO_4$: C, 61.60; H, 7.36. Found: C, 61.45; H, 7.25. IR (Nujol mull): 2008, 1931, 1913, 1888 cm^{-1} (all strong, ν_{CO}).

(7) X-ray structure determination for **1**: The crystal was taken straight from the mother liquor, coated in oil, and immediately frozen in a cold nitrogen stream. Diffraction was still quite weak. Data were collected at 173 K on an Enraf-Nonius CAD4 diffractometer. The compound ($C_{19}H_{27}VO_4$) crystallizes in the space group $P2_1/n$, with a = 8.525(2) Å, b = 26.637(8) Å, c = 8.920(2) Å, β = 103.42(2)°, V = 1973 $Å^3$, Z = 4, D_c = 1.25 g cm^{-3}, Mo Kα radiation (λ = 0.710 69 Å), μ = 5.0 cm^{-1}, and $F(000)$ = 784. A total of 2814 unique reflections were measured in the range $2° \le \theta \le 23°$, of which 1474 were considered observed ($|F^2| > 2\sigma(F^2)$). Non-H atoms were located by heavy-atom methods and refined anisotropically by full-matrix least squares, except C(6) and C(7), which became nonpositive definite when refined thus and were reset isotropic. Enraf-Nonius MolEN programs[17] and scattering factors from ref 18 were used. Hydrogen atoms were fixed in calculated positions. Final agreement factors were R = 0.073, R' = 0.070, and GOF = 1.3.

(8) Visser, J. P.; Schipperijn, A. J.; Lukas, J.; Bright, D.; deBoer, J. J. *J. Chem. Soc. D* **1971**, 1266.

(9) (a) Schmidbaur, H.; Schier, A.; Schubert, U. *Chem. Ber.* **1983**, *116*, 1938. (b) Nijveldt, D.; Vos, A. *Acta Crystallogr., Sect. B* **1988**, *44*, 296.

(10) de With, J.; Horton, A. D.; Orpen, A. G. *Organometallics* **1990**, *9*, 2207.

(11) (a) Hessen, B.; Teuben, J. H.; Lemmen, T. H.; Huffmann, J. C.; Caulton, K. G. *Organometallics* **1985**, *4*, 946. (b) Protasiewicz, J. D.; Bianconi, P. A.; Williams, I. D.; Liu, S.; Rao, C. P.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 4134.

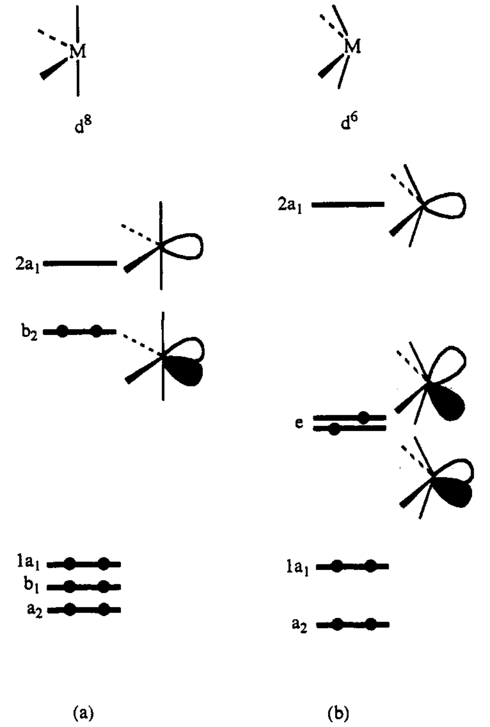
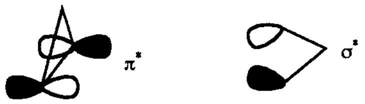


Figure 5. Frontier orbitals of the C_{2v} and C_{4v} ML_4 fragments.

defined by C(5)—C(6)—C(7), away from V.

In contrast to the solid-state structure described above, the metal–cyclopropenyl fragment of **1** appears to have 3-fold symmetry on the NMR time scale in solution. For example, the ^1H NMR spectrum of **1** in d_8-toluene solution consists of a singlet for the ^tBu groups and does not vary significantly between −80 and +70 °C. The resonance in the ^{13}C NMR spectrum corresponding to the quaternary ring carbons is, however, sharp only at low temperature and is broadened into the base line at 25 °C. Given that other features of the spectrum are not altered significantly over this range of temperature, we suggest that the ring carbons are being broadened at room temperature by the quadrupolar ^{51}V nucleus, which is "thermally decoupled" at low temperature. Hence, the C—V bonds in **1** must have a substantial amount of σ-character.[12]

The capacity of various metal fragments in cyclopropenyl complexes to progress toward complete insertion into a ring C—C bond has been investigated,[4] and the frontier orbitals of (a) C_{2v} ML_4 (d^8) and (b) C_{4v} ML_4 (d^6) fragments are sketched in Figure 5. Consider the complexes $[Ir(C_3Ph_3)Cl(CO)(PMe_3)_2][BF_4]$[13] and $[RhCl_2(PMe_2Ph)_2(C_3Ph_3)]$,[14] which are of type a. The interaction of the ligand π* orbitals with the metal b_2 orbital would lengthen the C—C bond and thus increase θ (Figure 4). This has the effect that the ligand σ* and π* orbitals become closer in energy[4] and increasing φ is favored because of better overlap with σ*.



As the ring opens up and φ approaches 180°, the interaction is entirely with σ*. In case b of the d^6 complex **1**, the ligand π* interacts with the half-filled e set, and the C—C bond is lengthened as before. In order to proceed further along the reaction profile of Figure 1, distortion of the carbonyl ligands from C_{4v} toward the C_{2v} geometry of the metallacyclobutadiene is required.[15] The subsequent transformation of the frontier orbitals to the type a of Figure 5 would leave the b_2 orbital (which is the primary bonding orbital with the ring fragment) empty, and so the insertion profile is arrested at the point observed.

Hence, almost complete scission of one of the C—C bonds in the carbocycle (as evidenced by the extremely long C—C bond) and concomitant V—C σ-bond formation (as evidenced by the short bond lengths and quadrupolar broadening of the ^{13}C NMR signals) have occurred in **1**. Further progression toward a metallacyclobutadiene configuration is prevented simply because of the fact that the metal center is formally only d^6. It would be interesting to see whether complete insertion of the V atom into the C—C bond could be facilitated by reduction of **1**. This is currently under investigation.

Acknowledgment. We wish to thank the Ramsay Memorial Fellowships Trust and the Royal Commission for the Exhibition of 1851 for a Ramsay Fellowship (to P.S.) and the EPSRC for support.

Supplementary Material Available: Tables of crystal data, atomic positional and equivalent isotropic displacement parameters, bond distances and angles, anisotropic thermal parameters, and least-squares planes and deviations therefrom for **1** (9 pages). Ordering information is given on any current masthead page.

OM9402731

---

(12) This type of behavior has been observed previously in (butadiene)niobium complexes which display metallacyclopentene character: Green, M. L. H.; Hughes, A. K.; McGowan, P. C.; Mountford, P.; Scott, P.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1992**, 1591.

(13) Tuggle, R. M., Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237.

(14) Frisch, P. D.; Khare, G. P. *Inorg. Chem.* **1979**, *18*, 781.

(15) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(16) Johnson, C. K. ORTEP II; Report ORNL-5738; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(17) Enraf-Nonius MolEN Structure Determination System, 1990.

(18) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.