Biscyclopentadienylvanadium(III) Cation: a d^2 Titanocene-like Stable Species; Generation and Reactivity

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Summary The generation of the $[V(cp)_2]^+$ unit (cp = η^5-C_5H_5) in basic solvents such as water, acetone (L), and pyridine (L) leads to the isolation of $[V(cp)_2L]^+[BPh_4]^-$ paramagnetic complexes, whose high π-basicity toward π-acids is shown by the ready carbonylation of aqueous solutions of $[V(cp)_2Cl]$ to give $[V(cp)_2(CO)_2]^+$ quantitatively.

Many interesting reactions of the highly reactive and elusive species $[Ti(cp)_2]$,[1] $[Mo(cp)_2]$, and $[W(cp)_2]$,[2] have been reported; of particular note are the d^2 biscyclopentadienyls $[Ti(cp)_2]$,[3] $[Ti(cp)_2(CO)_2]$,[4] $[Mo(cp)_2H_2]$,[5] and $[V(cp)_2I]$.[6] The chemistry of $[V(cp)_2]^+$, isoelectronic with metastable monomeric titanocene, is virtually unexplored. Previous studies on titanocene and other titanium species suggest that such a compound would be co-ordinatively unsaturated and highly reactive. Interest in the preparation of titanocene-like complexes results from a search for isolable compounds which would co-ordinate and promote reduction of molecular nitrogen.[1] The presence of $[V(cp)_2]^+$ in an aqueous solution was inferred from magnetic measurements showing two unpaired electrons per vanadium atom,[7] which referred to the electronic configuration of the unsolvated $[V(cp_2)]^+$ species.[8] $[V(cp)_2]Cl$ (I) in aqueous solution can be considered as a genuine source of $[V(cp_2)]^+$, the cation being precipitated as the tetraphenylborate derivative. Recrystallisation from acetone gave deep-blue crystals of $[V(cp)_2CO(Me)_2]^+[BPh_4]^-$, (II), ($\nu_{CO}$ 1660 cm^{-1}; μ_{eff} 2·93 B.M., 292 K). The reaction of (I) in tetrahydrofuran (THF) in the presence of pyridine (py) and $NaBPh_4$ gave blue-green crystals of $[V(cp)_2(py)]^+[BPh_4]^-$, (III), (μ_{eff} 2·76 B.M., 291 K). These results suggest that the magnetic moment reported for $[V(cp_2)]^+$ in aqueous solution, could be attributed to the monoaquo solvated species $[V(cp)_2(H_2O)]^+$, (IV). We were unable to obtain a material analysing correctly for $[V(cp)_2]^+[BPh_4]^-$, probably owing to the instability of the unsaturated 14-electron configuration of $V(cp)_2^+$, the more stable 16-electron species $[V(cp)_2L]^+$ [9] being favoured. Nevertheless, $[V(cp)_2]^+$ does not 'tautomerise' as both $[Ti(cp)_2]$[3] and $[Ti(Me_5C_5)_2]$[1] do, and remains intact through all the reactions.

The high π-basicity of the $[V(cp)_2]^+$ unit is illustrated by the reactions of (II) and (IV) with CO, which both give the known $[V(cp)_2(CO)_2]^+[BPh_4]^-$ (V),[10] quantitatively. The carbonylation of an aqueous solution of (I) appears to be the simplest synthetic route to (V). When a cold aqueous solution of $[V(cp)_2]Cl$ was treated with CO (2 h) at atmospheric pressure, the gas was rapidly absorbed (2 mol per vanadium atom), and the solution changed from blue to maroon. Addition of $NaBPh_4$ to this solution gave (V) (*ca.* 70%, recrystallised from acetone). An analogous reaction can be carried out with an acetone solution of (II). (I) does not react with CO under the same conditions in the absence of an ionising solvent.

The π-basicity of $[V(cp)_2]^+$ can be further shown by its reactivity with isocyanide and phosphine ligands. The reaction of (II) with $C_6H_{11}NC$ and $Ph_2PCH_2CH_2PPh_2$ gave $[V(cp)_2(C_6H_{11}NC)_2][PBh_4]$, (VI), [$\nu_{CN}$ (Nujol) 2120 and 2150 cm^{-1}, τ $[(CD_3)_2CO]$ 8·3 (20H, m, C_6H_{11}), 6·0 (2H, m, C_6H_{11}), 4·36 (10H, s, cp), and 2·8 (20H, m, BPh_4)] and $[V(cp)_2(Ph_2PCH_2CH_2PPh_2)][BPh_4]$, (VII), respectively. (VII) was diamagnetic in the solid state, but its slight solubility prevented n.m.r. measurements being made.

On treatment of (II) in THF solution of L (L = py, PEt_3, and $PBu^n{}_3$) with CO, we obtained the crystalline violet solids $[V(cp)_2COL]^+[BPh_4]^-$, (VIII) [ν_{CO} (Nujol) 1930 cm^{-1} (L = py); ν_{CO}(THF) 1950 cm^{-1}, τ ($[^2H_8]$-THF) 3·0 (20H, m, BPh_4), 5·1 (10H, d, cp) $J_{P,cp}$ 2·0 Hz, 9·0 (15H, bm, Et) (L = PEt_3); ν_{CO} (THF) 1950 cm^{-1}, $\tau[(CD_3)_2CO]$ 3·0 (20H, bm, BPh_4), 4·75 (10H, d, cp) $J_{P,cp}$ 2 Hz, 9·0 (27H, bm, Bu) (L = $PBu^n{}_3$)]. The distinction between the π-basicity of $V(cp)_2{}^+$ and σ-basicity of other d^2 complexes, such as $[Ti(cp)_2(CO)_2]$ and $[Mo(cp)_2H_2]$, must be stressed.

We thank S.N.A.M. Progetti (Milan) for support.

(*Received*, 8*th April* 1975; *Com.* 410.)

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