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Cyclopentadienylbis[methylaminobis(difluorophosphine)] vanadium: The First Fully Substituted Cyclopentadienylteracarbonylvanadium Derivative

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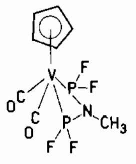
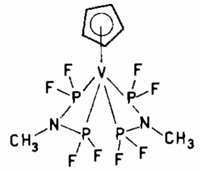
Recently the facile complete photochemical substitution of the six carbonyls in the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, and W) with $CH_3N(PF_2)_2$ was reported [1] to give relatively stable zerovalent metal complexes $[CH_3N(PF_2)_2]_3M$ (M = Cr, Mo, and W). We have found that a similar ultraviolet irradiation of $C_5H_5V(CO)_4$ with $CH_3N(PF_2)_2$ likewise results in complete substitution of the carbonyl groups to give $C_5H_5V[(PF_2)_2NCH_3]_2$, which is of significance in being the first cyclopentadienyltetracarbonylvanadium derivative in which all four carbonyl groups are replaced by trivalent phosphorus ligands. Previously reported reactions of cyclopentadienylvanadium carbonyls with trivalent phosphorus ligands [2–10] all result in the formation of tricarbonyls and dicarbonyls of the types $C_5H_5V(CO)_3L$ and $C_5H_5V(CO)_2L_2$.

A solution of 1.2 g (5.3 mmol) of $C_5H_5V(CO)_4$ [11] and 2.0 g (12 mmol) of $CH_3N(PF_2)_2$ [12] in 250 ml of diethyl ether was exposed for 90 minutes to the ultraviolet irradiation from a 450 watt mercury lamp in a water-cooled Pyrex immersion well. The infrared spectrum of the reaction mixture then showed the absence of ν(CO) frequencies. Removal of solvent followed by chromatography under nitrogen on a Florisil column in diethyl ether solution gave an orange band of $C_5H_5V[(PF_2)_2NCH_3]_2$. Elution of this band with diethyl ether gave 1.6 g (67% yield) of very air-sensitive orange $C_5H_5V[(PF_2)_2NCH_3]_2$, m.p. 93–94 °C, subl. 75–78 °C/0.1 mm, which could be purified further by low-temperature crystallization from pentane. *Anal.* Calcd. for $C_7H_{11}F_8N_2P_4V$: C, 18.7; H, 2.4; F, 33.8; N, 6.2. Found: C, 18.5; H, 2.4; F, 35.6; N, 6.2. The stoichiometry $C_5H_5V[(PF_2)_2NCH_3]_2$ was also indicated by its proton n.m.r. spectrum which in $CDCl_3$ solution exhibits cyclopentadienyl (τ 5.18: singlet) and methyl (τ 7.32: broad triplet, J ≈ Hz) resonances of 5:6 relative intensities.

The intermediate dicarbonyl $C_5H_5V(CO)_2(PF_2)_2NCH_3$ can be obtained by altering the relative quantities of reactants. Thus the ultraviolet irradiation of 2.3 g (10 mmol) of $C_5H_5V(CO)_4$ and 2.0 g (12 mmol) of $CH_3N(PF_2)_2$ in 250 ml of diethyl ether for 90 minutes followed by chromatography under nitrogen on Florisil in dichloromethane solution gave 2.3 g (69% yield) of very air-sensitive orange $C_5H_5V(CO)_2(PF_2)_2NCH_3$, m.p. 65–67 °C, subl. 50–55 °C/0.1 mm, which could be purified further by low-temperature crystallization from pentane. *Anal.* Calcd. for $C_8H_8F_4NO_2P_2V$: C, 28.3; H, 2.4; N, 4.1. Found: C, 27.7; H, 2.4; N, 4.3. The stoichiometry $C_5H_5V(CO)_2(PF_2)_2NCH_3$ was also indicated by its proton n.m.r. spectrum which in $CDCl_3$ solution exhibits cyclopentadienyl (τ 5.01: triplet, J ≈ 1.7 Hz) and methyl (τ 7.33: sharp triplet, J ≈ 11 Hz) resonances of 5:3 approximate relative intensities. The infrared spectrum of $C_5H_5V(CO)_2(PF_2)_2NCH_3$ in CH_2Cl_2 solution exhibits strong ν(CO) frequencies at 1947 and 1893 cm^{-1} of approximately equal relative intensities indicative of a *lat*-$C_5H_5M(CO)_2XY$ derivative [13].

The properties of the volatile and air-sensitive complexes $C_5H_5V(CO)_2(PF_2)_2NCH_3$ and $C_5H_5V[(PF_2)_2NCH_3]_2$ are consistent with their formulations as the $C_5H_5V(CO)_4$ substitution products I and II, respectively. The dicarbonyl I is completely analogous to other reported [4, 9, 10] $C_5H_5V(CO)_2L_2$ derivatives. However, the carbonyl-free II is the first known example of a $C_5H_5VL_4$ derivative (L ≠ CO).


I


II

The unprecedented ability of $CH_3N(PF_2)_2$ to displace all four carbonyl groups of $C_5H_5V(CO)_4$ undoubtedly arises from the unique combination of bidentate chelating ability, a small "bite", and high π-acceptor strength of this ligand. Furthermore, the reactions of $CH_3N(PF_2)_2$ with $C_5H_5V(CO)_4$ and $M(CO)_6$ (M = Cr, Mo, and W) which lead to the facile complete photochemical substitution of all carbonyl groups to form derivatives with biligate monometallic $CH_3N(PF_2)_2$ ligands are in contrast to the reactions of $CH_3N(PF_2)_2$ with cobalt [14] and iron [15] carbonyls which lead most readily to polymetallic derivatives in which metal–metal bonds are bridged by one to three $CH_3N(PF_2)_2$ ligands.

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