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Preliminary communication

HYDRIDE TRANSFER FROM VANADIUM HYDRIDES TO FULVENES: RING-SUBSTITUTED η^5-CYCLOPENTADIENYLCARBONYLVANADIUM COMPLEXES

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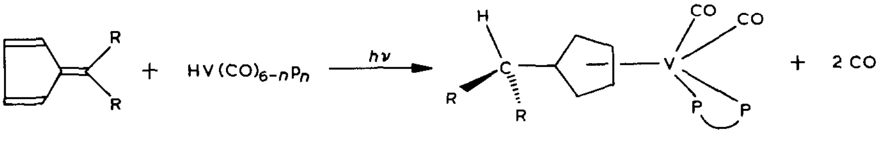
Summary

The fulvenes $C_5H_4CR_2$ (R = Me, Ph, p-C_6H_4OMe, p-$C_6H_4NMe_2$) react photochemically with $[VH(CO)_{6-n}p_n]$ (p_n = $Ph_2PCH_2PPh_2$, $Ph_2P(CH_2)_2PPh_2$, $MeC(CH_2PPh_2)_3$) to form *cis*-$[\eta^5$-$C_5H_4CHR_2V(CO)_2p_n]$.

While treatment of $[V(CO)_5THF]^-$ and $[V(CO)_5NO]$ with diphenylfulvene, $C_5H_4CPh_2$, leads to thermolabile $[V(CO)_5$-η^2-$C_5H_4CPh_2]^-$ and $[V(CO)_2$-η^6-$C_5H_4CPh_2(NO)]$, respectively [1], the hydrido complexes $[VH(CO)_{6-n}p_n]$ (n = 2, p_n = $Ph_2PCH_2PPh_2$: $p_2(1)$ and $Ph_2P(CH_2)_2PPh_2$: $p_2(2)$; n = 3, p_n = $MeC(CH_2PPh_2)_3$: Cp_3) readily transfer H^- to fulvenes $C_5H_4CR_2$ (R = Me, Ph, p-C_6H_4OMe, p-$C_6H_4NMe_2$), to yield the cyclopentadienyl derivatives *cis*-$[\eta^5$-$C_5H_4CHR_2V(CO)_2p_n]$ as the main product:



R = p_n	Me	Ph	p-C_6H_4OMe	p-$C_6H_4NMe_2$
$p_2(1)$		**1b**		
$p_2(2)$	**2a**	**2b**	**2c**	**2d**
Cp_3		**3b**		

As we have recently shown, the hydridovanadium complexes are readily accessible in excellent yields (90% and more) by ion exchange of $[Et_4N]$-$[V(CO)_{6-n}p_n]$ on silica gel [2—4].

Although the formation of ring-substituted η^5-cyclopentadienyl complexes from fulvenes and transition metal carbonyls in the presence of H^- transfer reagents such as $[AlH_4]^-$ has been known for more than twenty years [5,6], direct hydrogenation by transition metal hydrides is less common. In the carbonylvanadium system, hydride transfer to organic substrates has been described in several instances. Examples are the formation of $[HNEt_3]$-$[V(CO)_4p_2(2)]$ from the reaction between $[VH(CO)_4p_2(2)]$ and NEt_3 [2] (compare also "$[VH(CO)_6]$" in R_2O, which actually is $[HOR_2][V(CO)_6]$ [7]), various H/X exchange reactions between $[V(Cp)H(CO)_3]^-$ and RX (such as MeCOCl) [8], and the synthesis of η^3-allyl complexes by hydrogenation of 1,3-butadiene or isoprene with "$[VH(CO)_6]$" or $[VH(CO)_4LL]$ (LL = $p_2(1)$, $Ph_2As(CH_2)_2PPh_2$) [9]. A hydride intermediate $CpC(Me)CH_2{-}H{\cdots}V(CO)_6$ had also been postulated for the reaction between neutral $[V(CO)_6]$ and dimethylfulvene, which leads to an alkenyl substituted derivative η^5-$C_5H_4C(Me){=}CH_2V(CO)_4$ [10]. Several other ring-substituted derivatives of $[V(Cp)(CO)_4]$ are known, among them $[V(C_5H_4Et)(CO)_4]$ (from $[V(CO)_6]$ and 5-ethylcyclopentadiene) [10], $[V(C_5H_4Me)(CO)_4]$ [11] which is also formed in small amounts from $[V(CO)_6]$ and $C_5H_4CH_2$ [10], and $[V(C_5H_4C(O)Me)(CO)_4]$ [12]. We outline below a new, generally applicable route to phosphine-stabilized derivatives of $[V(Cp)(CO)_4]$ with a substituent on the Cp ring.

In a typical experiment, a solution of 1.25 g (2.28 mmol) $[VH(CO)_4p_2(1)]$ and 0.78 g (2.35 mmol) diphenylfulvene in 100 ml dry and oxygen-free THF, was irradiated for 2 h (high-pressure mercury lamp, quartz immersion well) with a weak N_2 stream passing through the solution, to form $[V(C_5H_4CHPh_2V$-$(CO)_np_2(1)]$ (n = 2 (**1b**) and n = 3 (4)). After removal of the solvent, the red-brown residue was dissolved in 15 ml toluene and transferred to a column filled with silica gel (70—230 mesh ASTM; pretreated under high vacuum and loaded with N_2). Elution with toluene/n-pentane 2/1 gave $[V(C_5H_4CHPh_2)(CO)_4]$ (6) and 4 (first fraction), unreacted $[VH(CO)_4p_2(1)]$ (second fraction), and finally a red fraction of **1b**. This solution was concentrated to 5 ml, treated with 15 ml n-pentane and set aside overnight at 0°C. The red-brown precipitate obtained was filtered off, washed with two 5 ml portions of pentane, and dried for 5 h (0.01 Torr, room temperature) to yield 320 mg (20%) of an air-sensitive, brown powder. Yields of the other (red to ochre) complexes were: **2a** (20%), **2b** (50%), **2c** (30%), **2d** (30%) and **3b** (15%).

IR and ^{51}V NMR data are listed in Table 1, which also includes some data for related compounds taken from the literature. In some cases, the tricarbonyl (4,5) and the tetracarbonyl species (6) are formed as by-products. The formation of a dinuclear $[\{V(C_5H_4CHPh_2)(CO)_3\}_2(\mu\text{-}p_2(1))]$ instead of a mononuclear species 4 can be excluded on the basis of the positions of the ^{51}V NMR signals of 4, $[V(Cp)(CO)_3p_2(1)]$ and $[\{V(Cp)(CO)_3\}_2(\mu\text{-}p_2(1)]$ (Table 1). In the untreated reaction mixture from $[VH(CO)_4p_2(2)]$ and $C_5H_4CR_2$ (R = Me, p-C_6H_4OMe, p-$C_6H_4NMe_2$), an additional IR absorption at 1742 cm^{-1} is observed, which compares with $\nu(CO)$ 1758 cm^{-1} for $[V(Cp)(CO)PhP$-$(CH_2CH_2PPh_2)_2]$ [15]. The downfield shift of $\delta(^{51}V)$ of the ring-substituted relative to the unsubstituted complexes (6 and $[V(Cp)(CO)_4]$, **2** and $[V(Cp)$-$(CO)_2p_2(2)]$, **1b** and $[V(Cp)(CO)_2p_2(1)]$), and of **1b** relative to **2b** is in accord with what one would expect from decreasing vanadium-ligand interaction with increasing steric hindrance (for discussion see ref. 13). This effect has also been

TABLE 1

IR AND ^{51}V NMR DATA

Complex [a]	ν(CO)	(cm^{-1})	Solvent	δ(^{51}V) [b] (ppm)
cis-[V(η^5-$C_5H_4CHPh_2$)$(CO)_2p_2(1)$] (**1b**)	1862	1800	toluene	−812
cis-[V(η^5-$C_5H_4CHMe_2$)$(CO)_2p_2(2)$] (**2a**)	1859	1787 [c]	THF	−1058
cis-[V(η^5-$C_5H_4CHPh_2$)$(CO)_2p_2(2)$] (**2b**)	1863	1791	THF	−1083
cis-[V(η^5-C_5H_4CH(*p*-$C_6H_4OMe)_2(CO)_2p_2(2)$] (**2c**)	1860	1788 [c]	THF	[d]
cis-[V(η^5-C_5H_4CH(*p*-$C_6H_4NMe_2)_2(CO)_2p_2(2)$] (**2d**)	1861	1790 [c]	THF	−1082
cis-[V(η^5-$C_5H_4CHPh_2$)$(CO)_2Cp_3$] (**3b**)	1862	1775	THF	[d]
[V(η^5-$C_5H_4CHPh_2$)$(CO)_3p_2(1)$] (**4**)	1945	1839	toluene	−1348
[V(η^5-$C_5H_4CHMe_2$)$(CO)_3p_2(2)$] (**5**)	1925	1840	THF	[d]
[V(η^5-$C_5H_4CHPh_2$)$(CO)_4$] (**6**)	2015	1910	toluene	−1507
[V(η^5-C_5H_5)$(CO)_4$] [e]	1919	2024	THF	−1534
[V(η^5-C_5H_5)$(CO)_3p_2(1)$] [f]	1950	1872	THF	−1340
[{V(η^5-C_5H_5)$(CO)_3$}$_2$(μ-$p_2(1)$)] [f]				−1299
cis-[V(η^5-C_5H_5)$(CO)_2p_2(1)$] [f]	1871	1809	THF	−860
cis-[V(η^5-C_5H_5)$(CO)_2p_2(2)$] [e]	1870	1799	THF	−1110

[a] Abbreviations: $p_2(1) = Ph_2PCH_2PPh_2$, $p_2(2) = Ph_2PCH_2CH_2PPh_2$, $Cp_3 = MeC(CH_2PPh_2)_3$. [b] Relative to $VOCl_3$, at 302(2) K. [c] A third absorption at 1742 cm^{-1} may be due to [V($C_5H_4CHR_2$)(CO)p_n]. [d] Not observed. [e] Ref. 13. [f] Ref. 14.

observed for δ(^{95}Mo) in several [Mo(η^6-arene)$(CO)_3$] complexes with methyl substituted benzenes [16].

The ^{1}H NMR spectral pattern (80 MHz), as exemplified for 2a (CH_3: 0.98, doublet: *J* 6.8 Hz; PCH_2P: 2.29; Me_2CH: 2.50, septet: *J* 6.8 Hz; Cp protons: 3.57 and 3.98; phenyl protons: 7.13 and 7.3—7.6 ppm) is consistent with the formulation as η^5-cyclopentadienyl with an unusually high electron density on the Cp ring.

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