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CARBONYL AND TRIFLUOROPHOSPHINE ADDUCTS OF BIS(2,4-DIMETHYLPENTADIENYL)TITANIUM AND BIS(2,4-DIMETHYLPENTADIENYL)VANADIUM

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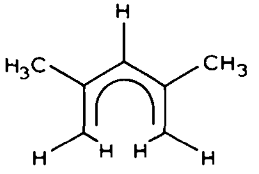
Summary

The syntheses of mono(carbonyl) and mono(trifluorophosphine) adducts of bis(2,4-dimethylpentadienyl)titanium and bis(2,4-dimethylpentadienyl)vanadium are described. Characterization has been achieved by routine spectral and analytical procedures. Detailed ^1H and ^{13}C NMR studies, as well as electron paramagnetic resonance and comparative infrared studies have been carried out in order to gain further understanding of the electronic nature of pentadienylmetal compounds, particularly compared to cyclopentadienylmetal compounds. Thus, infrared and EPR studies of $V(C_5H_5)_2(CO)$ and $V(2,4\text{-}C_7H_{11})_2(CO)$ suggest that the withdrawal of electron density by the 2,4-dimethylpentadienyl ligand is considerably greater than that by the cyclopentadienyl ligand

Recently we have demonstrated that the pentadienyl ligand and/or various methylated derivatives form a number of complexes of stoichiometry quite analogous to those of better known cyclopentadienyl compounds [1,2]. For example, the two series $M(2,4\text{-}C_7H_{11})_2$ ($2,4\text{-}C_7H_{11} = 2,4\text{-}(CH_3)_2C_5H_5$, I) and $M(C_5H_5)_2$ can now be compared for M = V, Cr, Fe, Ru [3]. While such comparisons (particularly with regard to their structural natures) now have provided much insight into these



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systems, much still remains to be learned regarding the relative reactivities of these two series. One classic mode of metallocene reactivity involves the coordination of various Lewis bases (e.g., CO or PF_3) to yield either mono-adducts (M = V [4], Cr [5]) or bis-adducts (M = Ti [6]). In order to gain an understanding of the relative reactivities of the $M(2,4\text{-}C_7H_{11})_2$ and $M(C_5H_5)_2$ compounds, and of the general chemical and electronic natures of the various adducts formed, we have investigated the reactions of the $M(2,4\text{-}C_7H_{11})_2$ compounds (M = Ti, V, Cr) with CO and PF_3.

Experimental

All operations involving organometallics were carried out under an atmosphere of prepurified nitrogen in Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each (generally involving Na/K, benzophenone) and were distilled under nitrogen immediately prior to use. Elemental analyses were obtained from Galbraith Laboratories. $M(2,4\text{-}C_7H_{11})_2$ complexes (M = Ti, V, Cr) were prepared as previously described [1,2]. Vanadocene [7] and vanadocene monocarbonyl [4] were prepared according to reported procedures, and purified by careful sublimation.

Spectroscopic studies. Infrared spectra were recorded on a Perkin–Elmer model 298 spectrophotometer. Mulls were prepared in a glovebox with dry, degassed Nujol. All infrared spectra were calibrated with polystyrene. Magnetic susceptibility measurements were carried out by the Evans method [8]. ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on Varian SC-300 and FT-80 spectrometers. ^1H NMR spectra are reported relative to TMS using C_5D_5H (δ 7.15 ppm) as internal standard. ^{13}C, ^{19}F, and ^{31}P NMR spectra are similarly referenced (vs. TMS, $CFCl_3$, and 85% H_3PO_4, respectively). Mass spectra were recorded on a Varian MAT 112 spectrometer or a VG Micromass 7070 double focusing high resolution mass spectrometer with VG Data System 2000 at 70 eV. Except for the parent fragment, peaks are quoted only if their relative intensities are at least 10% of the intensity of the strongest peak. The PF_3 adducts did not display parent peaks.

Bis(2,4-dimethylpentadienyl)titanium mono(trifluorophosphine), $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$. $Ti(2,4\text{-}C_7H_{11})_2$ was prepared as a solution in pentane as previously outlined [1c]. Exposure of this solution to gaseous PF_3 led to immediate reaction, as evidenced by the change in solution color from deep emerald green to a lime green (almost yellow-green). Depending on the initial concentration of $Ti(2,4\text{-}C_7H_{11})_2$ in pentane, some product may precipitate at this point. Cooling the solution or mixture to −78°C leads to crystallization of the product, which is reasonably pure at this point but may be further purified by sublimation (ca. 50°C).

Complete infrared data (Nujol mull): 1032m, 1025m, 1000m, 895m, 880mw, 864mw, 854mw, 847sh, 807s, 790s, 781s cm^{-1}. Anal. found: C, 51.04; H, 6.83. $C_{14}H_{22}F_3PTi$ calcd.: C, 51.55, H, 6.80%.

^1H NMR: δ 4.76 (s, 1H), 2.42 (s, 2H), 1.36 (s, 6H), 0.64 (d of d, J 14, 4.5 Hz.) ppm. ^{13}C NMR: δ 116.5 (s), 102.1 (d, J 166 Hz.), 55.0 (t of d, J 13, 158 Hz), 29.1 (q, J 125 Hz.). ^{19}F NMR: 21.8 ppm upfield (d, J(PF) 1340 Hz.). ^{31}P NMR: 209.6 ppm downfield (q, J(PF) 1340 Hz).

Bis(2,4-dimethylpentadienyl)vanadium mono(trifluorophosphine), $V(2,4\text{-}C_7H_{11})_2(PF_3)$. This compound was prepared by a manner strictly analogous to that used for the corresponding titanium compound. A color change from deep green to blue-green took place. While crystallization of this compound leads to a reasonably pure product, sublimation can also be utilized.

Complete infrared data (Nujol mull): 3032mw, 1498sh, 1283mw, 1163w,br, 1024ms, 997ms, 934m, 919mw, 885ms, 869m, 813s, 795s, 783s, 745ms, 726sh cm^{-1}. Anal. Found: C, 51.45; H, 6.56. $C_{14}H_{22}F_3PV$ calcd.: C, 51.07; H, 6.74%. Magnetic susceptibility (Evans method): 1.6 μ_B (THF).

Bis(2,4-dimethylpentadienyl)vanadium monocarbonyl, $V(2,4\text{-}C_7H_{11})_2CO$. A variable quantity of $V(2,4\text{-}C_7H_{11})_2$ is dissolved in a small volume of hexane (in fact, crude extracts from the original preparation of $V(2,4\text{-}C_7H_{11})_2$ can generally be used), and exposed to an excess of gaseous CO. A rapid change in the shade of green occurs, leading to formation of the product. Cooling to −78°C leads to deep green, needle-shaped crystals of product. After removing the supernatant by syringe, the crystals are dried first by draining at −78°C, followed by final evaporation in a dry nitrogen stream. If desired, the product may be further purified by sublimation (ca. 50°C).

Complete infrared data (Nujol mull): 3027w, sh, 1942s, 1025mw, 1004w, 994w, 860w, 723w cm^{-1}. Anal. Found: C, 66.75; H, 8.42. $C_{15}H_{22}OV$ calcd.: C, 66.91; H, 8.24%. Magnetic susceptibility (Evans method): 1.7 μ_B (THF).

Mass spectrum: *m/e*, %: 51, 85%; 55, 15%; 76, 12%; 90, 52%; 91, 11%; 103, 11%; 116, 13%; 129, 18%; 130, 12%; 142, 19%; 143, 100%; 144, 49%; 233, 22%; 235, 75%; 236, 15%; 237, 75%; 238, 13%; 241, 72%; 242, 12%; 269, 7%.

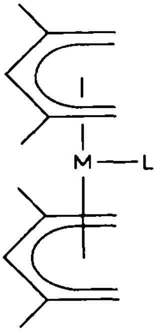
Results and discussion

The reaction of $M(2,4\text{-}C_7H_{11})_2$ (M = Ti,V) with CO or PF_3 leads to the very rapid formation of monobase adducts as in eq. 1. While the previously reported $Ti(2,4\text{-}C_7H_{11})_2CO$ complex is thermally unstable, the remaining members of this series are reasonably stable and can be sublimed slightly above room temperature (at ca. 50°C). The compounds are slightly air-sensitive and are reasonably soluble in many organic solvents. When the above reactions are attempted for the M = Cr complex, no adducts appear to be formed [9].

$$M(2,4\text{-}C_7H_{11})_2 + L \rightarrow M(2,4\text{-}C_7H_{11})_2(L) \qquad (1)$$

$$(M = Ti,\ V;\ L = CO,\ PF_3)$$

The formulation of these compounds as monobase adducts follows straightforwardly from analytical, infrared, NMR, and EPR data. The analytical data in each case fit well with that expected for a 1/1 adduct. The infrared spectra of the monocarbonyl adducts are particularly diagnostic in that they each display a single peak attributable to a carbonyl stretching frequency at 1942 cm^{-1}. Further, the NMR spectra of $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$ and the EPR spectra of $V(2,4\text{-}C_7H_{11})_2(PF_3)$ each demonstrate splittings arising from the presence of a single phosphorus nucleus. The formation of 17 electron $V(2,4\text{-}C_7H_{11})_2(L)$ (L = CO, PF_3) complexes is not surprising in view of the fact that the corresponding 17 electron $V(C_5H_5)_2(CO)$ complex is known [4]. However, the formation from $Ti(2,4\text{-}C_7H_{11})_2$ of only 16 electron monobase adducts contrasts markedly with the situation known for the corresponding cyclopentadienyl and pentamethylcyclopentadienyl systems, where only 18 electron dicarbonyl and bis(trifluorophosphine) adducts are known. The ^1H and ^{13}C NMR spectra are particularly useful in understanding the origin of this difference. While $Ti(2,4\text{-}C_7H_{11})_2$ exhibits seven resonances in both the ^1H and the ^{13}C NMR spectra (indicative of equivalent ligands in an unsymmetric environment), [1c,10] only four resonances are observed for the 2,4-dimethylpentadienyl ligands in the monobase adducts. Since these adducts are certainly more crowded than the (already crowded) $Ti(2,4\text{-}C_7H_{11})_2$ complex, it is unreasonable to assume a lower barrier to ligand oscillation. Rather, it must be assumed that the ligands are present in a more symmetric environment, such as II. This is also in agreement with the ^1H and ^{13}C NMR spectra of $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$. In the ^1H spectrum one observes



(II)

splitting of the H_{endo} on the terminal carbon atom protons into a doublet by the phosphorus nucleus ($I = 1/2$, J 14 Hz.). An analogous splitting is also observed for the terminal carbon atoms (in the 1 and 5 positions, J(CP) 13 Hz.) in the proton decoupled ^{13}C NMR spectrum (Fig. 1). The preferential splitting of the H_{endo} and C(1,5) atoms which reside by the open ligand faces is in line with the placement of the PF_3 ligand in their proximity, as in II, since through-space interactions can become significant in crowded molecular complexes [11].

It is evident, therefore, that very little room is available in these complexes for supplemental coordination of Lewis bases. In fact, even $V(2,4\text{-}C_7H_{11})_2$ exhibits significant ligand crowding in the solid state [2a]. For several reasons it would seem that the "bent sandwich" $M(C_5H_5)_2L_n$ and $M(C_5(CH_3)_5)_2L_n$ complexes so prolific for first row transition metals will have no counterpart in at least the first row transition metal-pentadienyl systems. First, these ligands are substantially wider than either the C_5H_5 or $C_5(CH_3)_5$ ligands, and thus the ligand plane must be closer to the metal atom than the C_5H_5 or $C_5(CH_3)_5$ ligand planes. Further, the V–C and Ti–C bond distances are considerably shorter in the low spin "open" systems as compared to the latter two closed systems [2b,12]. However, substantially larger metal systems might exhibit something akin to the "bent sandwich" configurations [13].

Some significant electronic information can be obtained by a comparison of $V(C_5H_5)_2(CO)$ with $V(2,4\text{-}C_7H_{11})_2CO$ since the carbonyl ligand is a good indicator of relative donor/acceptor abilities for other ligands in a metal complex. It turns out that while $V(C_5H_5)_2(CO)$ has ν(CO) 1881 cm^{-1}, $V(2,4\text{-}C_7H_{11})_2(CO)$ is char-

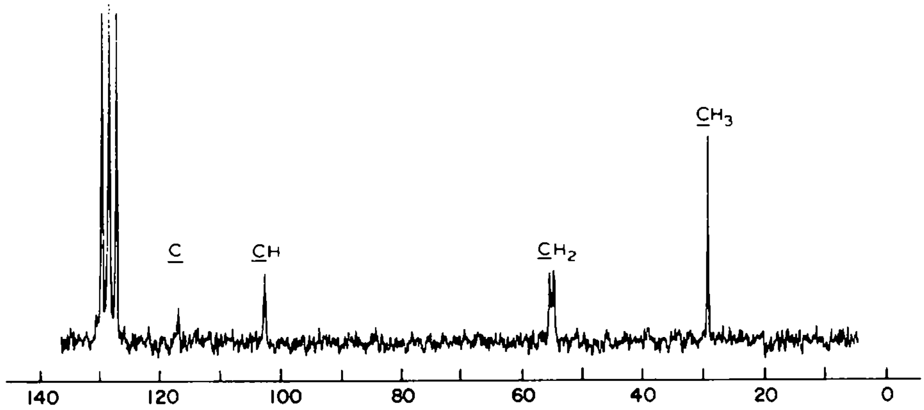


Fig. 1. Proton decoupled ^{13}C nuclear magnetic resonance spectrum of $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$ in benzene-d_6.

acterized by $\nu(CO)$ 1942 cm^{-1}. Two explanations seem possible, one being steric while the other is electronic. With regard to the steric possibility, it has already been observed that $V(2,4\text{-}C_7H_{11})_2$ is a crowded molecule. Thus, as a monocarbonyl adduct is formed, it is possible that the CO ligand is sterically hindered from making a close approach to the vanadium atom, and hence the extent of interaction is reduced. However, $Mn(C_5H_7)(CO)_3$ [14] also possesses a notably higher C–O stretching frequency than $Mn(C_5H_5)(CO)_3$ [15], and therefore it appears that this is actually a general electronic trend. In this regard, one would have to say that the 2,4-dimethylpentadienyl ligand has acquired more negative charge and the metal atom more positive charge, than their counterparts in $V(C_5H_5)_2(CO)$. Conceivably this could come about as a result of greater "δ" M → pentadienyl bonding. In fact, such "δ" bonding was observed in theoretical calculations to be substantially enhanced in the "open ferrocenes" as compared to ferrocene, and would seem to be necessary to account for the eclipsed nature of $Fe(2,4\text{-}C_7H_{11})_2$ in view of the presence of apparently severe interligand repulsions [16]. Alternatively or in conjunction with the above, reduced π pentadienyl → M bonding could contribute. However, it should be clear that any definite conclusions must await the completion of further detailed studies.

Also worthy of note are the electron paramagnetic resonance spectra. The room temperature solution spectrum of $V(2,4\text{-}C_7H_{11})_2(CO)$ displays an eight line pattern characterized by an isotropic g value of 1.992, and a vanadium hyperfine ($I = 7/2$) splitting of 79.4 G (G = Gauss) in THF. These values are not unlike those for $V(2,4\text{-}C_7H_{11})_2$ itself [17]. The spectrum of $V(2,4\text{-}C_7H_{11})_2(PF_3)$ is similar, having a g value of 1.991 (toluene) and a vanadium hyperfine splitting of 77.1 G, but also demonstrates splitting by the phosphorus nucleus (53.6 G). To gain further direct comparisons between cyclopentadienyl and pentadienyl systems, the EPR spectrum of the known compound $V(C_5H_5)_2(CO)$ was obtained, which was characterized by a g value of 2.009 and a relatively small vanadium hyperfine splitting of 27.8 G. Most likely this small value indicates more delocalization of the unpaired electron density from the vanadium atom in $V(C_5H_5)_2(CO)$ compared to $V(2,4\text{-}C_7H_{11})_2(CO)$ [18]. Under this assumption, a consistent but tentative correlation can be made. The infrared results described above demonstrate that the carbonyl ligand in

$V(C_5H_5)_2(CO)$ has absorbed more electron density than the carbonyl ligand in $V(2,4\text{-}C_7H_{11})_2(CO)$. One might imagine, then, that in response to this greater charge drain by the $2,4\text{-}C_7H_{11}$ ligand, the (more positively charged) vanadium atom becomes more resistant to delocalization of the unpaired electron, or of the electrons available for backbonding to the carbonyl ligand. It would seem then that taken together, the infrared and EPR spectral results suggest a noticeably greater reluctance on the part of vanadium(II) in $V(2,4\text{-}C_7H_{11})_2(CO)$ (as compared to $V(C_5H_5)_2(CO)$) to share its *d* orbital electron density with its additional ligands. It is anticipated that further studies in this area will shed more light on the precise energetics behind these observations, and these are presently being pursued.

Acknowledgments

It is a pleasure to express our gratitude to Professor Jeffrey L. Peterson of West Virginia University for his help in simulating the EPR spectrum of $V(2,4\text{-}C_7H_{11})_2(PF_3)$, and for several helpful discussions. It is also a pleasure to express our thanks to the National Science Foundation (Grant ♯ CHE-8120683), the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant ♯ 14223-ACI), and to the University of Utah Research Committee for their support. We would also like to acknowledge the National Science Foundation (Grant CHE-8100424) and the University of Utah Institutional Funds Committee for providing funds for the departmental purchase of the Mass Spectrometer System.

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9 One might attribute the lower reactivity of $Cr(2,4\text{-}C_7H_{11})_2$ to the shorter metal–ligand separation, or perhaps to its greater electron configuration. It should be noted that while $V(C_5H_5)_2(CO)$ and $Cr(C_5H_5)(CO)$ both exist, the vanadium complex is more resistant to CO dissociation.
10 As already reported [1c], these resonances occur at 125.1, 122.3, 116.6, 72.8, 71.9, 31.5, and 29.0 ppm, somewhat downfield of the resonances found for $Ti(2,4\text{-}C_7H_{11})_2(PF_3)$.
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17 (a) For $V(2,4\text{-}C_7H_{11})_2$, $g = 2.001$, hyperfine splitting = 77.2 G in THF [15b]; (b) J.-Z. Liu and R.D. Ernst, unpublished data.

18 A referee has correctly pointed out that a greater metal 4*s* contribution to the HOMO in the $V(C_5H_5)_2(CO)$ system could also be responsible for its smaller vanadium hyperfine coupling constant. While this may be true, the differences observed in coupling constants (79.4 vs. 27.8 G) seem large enough that they probably reflect at least partially a significant difference in electron delocalization, and this difference can be correlated with the infrared spectroscopic trends. Nevertheless, further studies to more precisely explain these data are in progress,