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Olefin and CO Competition Equilibria for Bis(cyclopentadienyl)vanadium(II)

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The substitution reactions of $VCp_2(CO)$ with some selected olefins have been studied. Tetracyanoethylene (tcne) and fumaronitrile (fn), containing electron-withdrawing substituents, promptly react with $VCp_2(CO)$ with quantitative formation of $VCp_2(tcne)$ and $VCp_2(fn)$, respectively, while acrylonitrile and diethyl fumarate (defu) gave partial displacement of coordinated carbon monoxide under a CO atmosphere. No CO displacement from $VCp_2(CO)$ was observed with cyclooctene and norbornene. The carbonylation of $VCp_2(defu)$ ($VCp_2(defu) + CO \rightleftarrows VCp_2(CO) + defu$) has been studied gas volumetrically from both sides, and the equilibrium constant for the displacement of coordinated defu by carbon monoxide was estimated to be 55 ± 8 at 298.5 K. Variable-temperature experiments between 298.5 and 327.7 K have shown the enthalpy change to be -2.4 kcal mol^{-1}. The equilibrium constant for the addition of defu to VCp_2 ($VCp_2 + defu \rightleftarrows Cp_2(defu)$) has been evaluated spectroscopically to be 150 ± 11 at 298.5 K. From the available data, the equilibrium constant for the addition of carbon monoxide to VCp_2 ($VCp_2 + CO \rightleftarrows VCp_2(CO)$) has been calculated to be $K_a = (8.2 \pm 0.4) \times 10^3$: i.e., about 2 orders of magnitude higher than that for the complexation of defu. The present data for the $3d^3$ system of vanadium(II) ($\tilde{\nu}_{CO}$ in toluene 1881 cm^{-1}) are compared with those exhibited by the $5d^{10}$ system of AuCl(CO) ($\tilde{\nu}_{CO}$ in toluene 2153 cm^{-1}), whose behavior consistently shows an opposite dependence, as far as the olefin/CO competition is concerned, on the nature of the olefin.

Introduction

Coordination of CO and olefins to transition-metal centers is an interesting subject [1,2] in connection with the catalytic processes involving both reagents such as hydroformylation, hydroesterification, and CO/olefin copolymerization. Thus, the evaluation of the CO/olefin competition within a given metal center is a fundamental acquisition for a better understanding of these processes.

Metal carbonyls have frequently been used as starting materials for the preparation of olefin derivatives.[3] However, a limited number of quantitative data have been reported on equilibria such as (1), all examples pertaining to metal complexes toward the end of the n*d* transition series.[4]

$$ML_n(\text{olefin}) + CO \rightleftarrows ML_n(CO) + \text{olefin} \qquad (1)$$

In a study of the olefin displacement in $Rh(acac)(C_2H_4)_2$ by CO,[4a] the constant of the substitution equilibrium was found to be above 100, thus showing that the carbonyl compound is largely favored with respect to the olefin adduct. Markó and co-workers[4b] reported that *dienes* are displaced from $Co_2(CO)_6(\eta^4\text{-diene})$ by CO (eq 2), with equilibrium constants in octane at 35 °C of 4.0×10^4 M^{-1} (diene = 1,3-cyclohexadiene) or 1.5×10^3 M^{-1} (diene = norbornadiene).

$$Co_2(CO)_6(\eta^4\text{-diene}) + 2CO \rightleftarrows Co_2(CO)_8 + \text{diene} \qquad (2)$$

$$\text{diene} = \text{1,3-cyclohexadiene, norbornadiene}$$

Photochemically generated[5] $Cr(CO)_5$(*cis*-cyclooctene) and thermally synthesized *cis*-$PtX_2(CO)$(olefin) (olefin = ethylene, propylene, cyclopentene, cycloheptene)[6] undergo substantially quantitative olefin substitution by CO to $Cr(CO)_6$ and *cis*-$PtX_2(CO)_2$, respectively.[7] Ligated carbon monoxide in a pyrazolylborato complex of copper(I), $Cu(HBpz_3)CO$,[8a] was reported to be dis-

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placed by olefins under unspecified conditions and for preparative purposes, a point which apparently has not been further investigated.[8b] Furthermore, in a study of the palladium(II)-catalyzed copolymerization of CO and ethylene, Brookhart and co-workers found that the 1,10-phenanthroline (phen) cationic ethylene complex $[Pd(phen)Me(C_2H_4)]^+$ undergoes ethylene displacement to the corresponding carbonyl derivative with an equilibrium constant of 2.2×10^5 at 298 K.[4c]

At the extreme right-hand side of the transition series, quantitative data are available for the $5d^{10}$ system of gold(I). The chloro carbonyl derivative AuCl(CO) does not react[4e] with olefins containing electron-withdrawing substituents such as acrylonitrile and tetracyanoethylene. However, partial CO displacement was observed with norbornene (nbn) to give AuCl(nbn), the equilibrium constant for the displacement of the complexed olefin by CO (AuCl(nbn) + CO $\rightleftarrows$ AuCl(CO) + nbn) being $K = 2.5 \times 10^{-1}$ at 21.5 °C,[4e] which implies a slightly higher stability of the olefin complex. In this connection it is important to note that the chloro carbonyl complex of gold(I) is characterized[4g] by a high $\tilde{\nu}_{CO}$ band at 2153 cm^{-1} in toluene, thus suggesting little, if any, π back-donation.

The available data suggested that within the domain of noble metals, and for the closed-shell 5d electronic configuration, the coordinating power of some unsubstituted monoolefins becomes comparable to that of CO, while olefins containing electron-withdrawing substituents have no tendency to bind. This behavior appeared to be intriguing and of sufficient interest to justify a further exploration of the CO/olefin competition in the domain of early transition elements. In this connection, we thought that vanadocene, VCp_2, might be a useful system, due to the fact that it is known to afford isolable compounds with both CO[9] and olefins bearing electron-withdrawing substituents, namely acrylonitrile, acrolein, crotonaldehyde, and methyl vinyl ketone, the last four products being obtained by reacting VCp_2 with the appropriate functionalized olefin, as shown in Scheme 1.[10] Moreover, the carbonyl adduct $VCp_2(CO)$ presents a carbonyl stretching vibration at 1881 cm^{-1} in toluene solution, suggesting a considerable degree of π back-donation. Thus, the thermodynamics of the addition reactions to vanadocene and the CO/olefin exchange on this $3d^3$ system (see Scheme 1) were anticipated to be highly informative.

Scheme 1. Equilibria between Vanadocene Derivatives and CO or Olefin

$$VCp_2 + L \rightleftarrows VCp_2L$$

$$L = CO, \text{olefin}$$

$$VCp_2(\text{olefin}) + CO \rightleftarrows VCp_2(CO) + \text{olefin}$$

In this paper we report the reaction of $VCp_2(CO)$ with olefins, showing that the products are strongly influenced by the nature of the substituents on the olefin, and we also present the thermodynamic data for one selected system. We believe these data to be of interest per se, beside being useful for a quantitative evaluation of the CO/olefin competition within a given metal center, and for a better understanding of closely related phenomena, such as poisoning by CO in the metal-catalyzed olefin polymerization.[11]

Results and Discussion

Synthesis of Vanadium Complexes. The research was initiated with a study of the system VCp_2/CO/(unsubstituted olefin). Initially cyclooctene was considered, i.e. the olefin which had been investigated more extensively for the gold(I) system, as far as the crystallographic data are concerned.[4e] However, cyclooctene was found to be unreactive toward VCp_2 and no carbonyl displacement was observed, thus suggesting that the carbonyl complex is largely favored. Norbornene, the olefin that had provided the gas volumetric equilibrium data with AuCl(CO),[4e] was equally unreactive toward $VCp_2(CO)$.

Earlier literature had established the synthesis of some vanadium olefin complexes (from VCp_2 and diethyl fumarate or diethyl maleate)[12] and the crystal and molecular structure[13] of the adduct of bis(cyclopentadienyl)vanadium with diethyl fumarate (defu), $VCp_2(defu)$, showing the vanadium atom to be η^5-coordinated to the two Cp rings and η^2(C,C)-bonded to the olefinic ligand. Moreover, some reactions of VCp_2 with olefins L containing electron-withdrawing substituents (L = acrylonitrile, acrolein, crotonaldehyde, methyl vinyl ketone) had been reported to give the adducts $VCp_2(L)$.[10] This led us to think that the study of the reactions of $VCp_2(CO)$ with olefins containing electron-withdrawing substituents could be a viable method for assessing the CO/olefin competition for this system of vanadium(II). This has been preceded by the synthesis of some new complexes of the type VCp_2(olefin), to assess the best system for this study.

It has been shown that 1 equiv of tetracyanoethylene (tcne) reacts at room temperature with $VCp_2(CO)$ in toluene solution, giving a dark brown solid that is almost insoluble in toluene or THF, which has been characterized analytically and spectroscopically as VCp_2(tcne) (**1**). Our structural proposal for this compound (vide infra) is based essentially on IR spectroscopy. Metal complexes containing tcne bonded through the carbon−carbon bond have been reported,[14] whose IR spectra, as expected for this type of bonding, show a small shift (5−10 cm^{-1}) of the CN stretching vibration with respect to the uncomplexed ligand. On the other hand, coordination through the nitrogen atom[15] causes large shifts (50−60 cm^{-1}) of the CN stretching vibration to lower wavenumbers. It is worth noting that the

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Chart 1. Schematic View of VCp_2(tcne) (1)

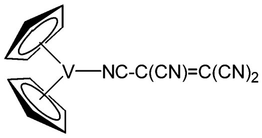
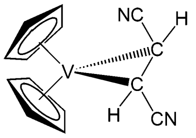


Chart 2. Schematic View of VCp_2(fn) (2)



vanadium derivatives of general formula VCp_2X(tcne) (X = Cl, Br, I),[16] which are characterized by four CN stretching vibrations between 2211 and 2128 cm^{-1}, contain the planar monodentate N-coordinated tcne ligand, as shown by an X-ray diffractometric study on VCp_2Br(tcne).[16] An absorption of medium intensity at 1400 cm^{-1} was assigned to the carbon−carbon stretching vibration of coordinated tcne. Similarly, VCp_2(tcne) of the present study shows bands at 2216 w, 2173 m, 2154 m, 2012 vs, and 1358 m-w cm^{-1}, thus suggesting a similar monodentate coordination of the ligand, as shown in Chart 1. CNDO/2 calculations[16] have indicated that the reduction of tcne to $[tcne]^-$ causes a shift of the olefin stretching vibration from 1570 to 1370 cm^{-1}. On this basis, we assign the band of medium intensity at 1358 cm^{-1} to the carbon−carbon stretching of the coordinated olefin. The oxidation state III can therefore be assigned to our tcne derivative of vanadocene.

A fast reaction has also been observed between either VCp_2 or VCp_2(CO) and fumaronitrile (fn). The brown solid, identified analytically and spectroscopically as VCp_2(fn) (**2**) shows only one absorption at 2188 cm^{-1}, assigned to the IR-active CN asymmetric stretching vibration of the coordinated fumaronitrile. An η^2 mode of bonding of fumaronitrile through the olefinic carbon−carbon bond is consistently suggested for **2**, as shown in Chart 2.

It should be noted that a similar coordination to vanadium has been reported for the structurally characterized diethylfumarato (defu) complex.[13]

CO/Olefin Competition Studies. The VCp_2(CO)/VCp_2(olefin) interconversion was studied by measuring the uptake of CO by VCp_2(olefin) or the CO evolution from VCp_2(CO) by operating at a constant atmospheric pressure of CO. Treatment of a toluene solution of VCp_2(CO) with 1 equiv of acrylonitrile in a gas volumetric apparatus[17] led to CO evolution up to a CO/V molar ratio of 0.014 at 295 K. On the other hand, VCp_2(acrylonitrile), independently prepared by addition of acrylonitrile to VCp_2,[10] absorbed CO up to a CO/V molar ratio of 0.835, under the same experimental conditions (see eq 3).

$$VCp_2(\text{acrylonitrile}) + CO \rightleftarrows VCp_2(CO) + \text{acrylonitrile} \quad (3)$$

Due to the gas volumetric imbalance of the forward and reverse experiments, acrylonitrile appeared to be inappropriate for a quantitative evaluation of the equilibrium, over extended periods of time and/or at higher temperatures, due to a possible parasitic, metal-catalyzed formation of polyacrylonitrile. It was therefore decided to study the behavior of a different olefin, namely diethyl fumarate (defu), with the carbonyl vanadium(II) derivative. Preliminary gas volumetric experiments carried out at 301 K with stoichiometric quantities of defu had in fact shown that the volumes of CO in the forward and reverse reaction almost exactly matched. This experimental observation, together with the fact that the uncomplexed diester and its vanadium adduct are easier to purify and to store than the corresponding acrylonitrile derivative, prompted us to study the competitive equilibrium between CO and defu (see eq 4)

$$VCp_2(\text{defu}) + CO \rightleftarrows VCp_2(CO) + \text{defu} \quad (4)$$

$$K_4 = [VCp_2(CO)][\text{defu}]/[VCp_2(\text{defu})][CO]$$

by measuring the CO evolved in starting from VCp_2(CO) and that absorbed by VCp_2(defu). Moreover, the literature had already shown[12] that the same product, VCp_2(defu), was obtained from VCp_2 by starting from either one of the two geometrical isomers of the olefin, diethyl maleate or defu. Thus, by using the latter olefin, no important rearrangements were anticipated to occur within the olefinic fragment upon interaction with vanadium, thus simplifying the analysis of the thermodynamic data.

The equilibrium was studied from both sides, i.e. both the CO absorption (forward reaction, K_4) by VCp_2(defu) and the carbon monoxide displacement from VCp_2(CO) (reverse reaction, $K_{-4} = 1/K_4$). Due to the fact that VCp_2(CO) is considerably favored with respect to VCp_2(defu) with equimolar concentrations of the nongaseous reagents, we used a high defu/V molar ratio in order to convert as much as possible of the starting material. By the methods described in the Experimental Section, the data reported in Table 1 have been obtained.

From the data of Table 1, the following can be concluded.

(i) The carbonyl derivative VCp_2(CO) is the thermodynamically favored compound at an atmospheric pressure of CO, the experimentally measured K_4/K_{-4} ratio being 3200 at 298.5 K.

(ii) Equilibrium 4 is not greatly affected by temperature between 298.5 and 327.7 K (see Figure 1, showing a van't Hoff plot of the equilibrium constants) thus implying a relative small value of ΔH. ΔH is estimated to be +1.7 kcal mol^{-1}, slightly endothermic in the direction of VCp_2(CO) being decarbonylated to give VCp_2(defu), with a small negative entropy contribution ΔS of −2.2 cal mol^{-1} K^{-1}. Such a negative contribution is rather surprising, due to the fact that 1 mol of CO is released in the process. Nevertheless, examples of reactions which produce H_2[18] or ethylene[4a] and are characterized by a negative entropy contribution are known in the literature. In those cases, translational and vibrational contributions have been considered to

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Table 1. Forward and Reverse Constants for Equilibrium 4, $VCp_2(defu) + CO \rightleftarrows VCp_2(CO) + defu$, at Different Temperatures[a,b]

T (K)	K_4	10^2K_{-4}
298.5	55 ± 8	1.7 ± 0.4
308.1	50 ± 9	1.8 ± 0.5
317.7	42 ± 8	2.0 ± 0.5
327.7	39 ± 6	2.2 ± 0.5

[a] The temperature was constant within ±0.1 °C, K_4 and K_{-4} originating from independent experiments. The quality of the experimental data can be evaluated by considering that the equilibrium constants are related by the expression $1/K_4 = K_{-4}$. [b] The enthalpy changes corresponding to the forward and reverse reactions are −2.4 and +1.7 kcal mol^{-1}, respectively.

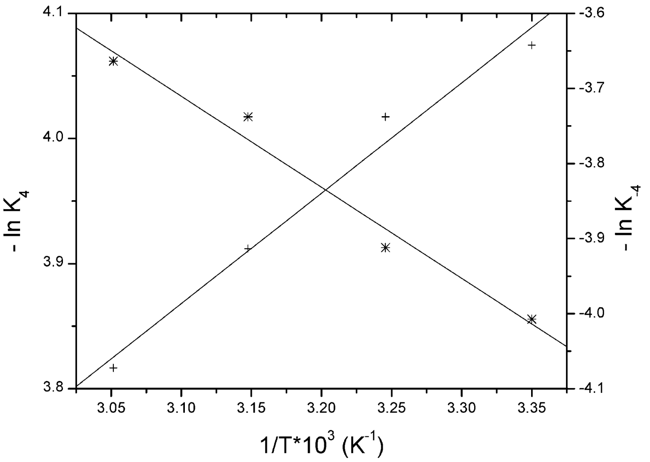

Figure 1. van't Hoff plots for equilibrium 4, $VCp_2(defu) + CO \rightleftarrows VCp_2(CO) + defu$ (K_4/K_{-4}). The symbols * and + refer to the forward and reverse reactions, respectively.

be important in defining the entropy change, especially when coordination of large molecules occurs.[19] In the present case, defu certainly loses degrees of freedom on going from solution to the rather constrained bonding situation in the metal complex.

As K_4 and K_{-4} are both independently measured quantities, it is possible to estimate the relative affinity of CO and defu for vanadocene. As shown in Scheme 2, reaction 4 is the sum of eqs a and b, and $K_4 = K_aK_b$. Since K_4 is known, by measuring the equilibrium constant of reaction b, it was anticipated that the third value, K_a, would become available, thus giving individual values for the addition of both CO and defu to vanadocene.

Scheme 2. Carbonylation of VCp_2 (a) and defu Dissociation from VCp_2(defu) (b)

$$VCp_2 + CO \rightleftarrows VCp_2(CO) \qquad (a)$$

$$K_a = [VCp_2(CO)]/[VCp_2][CO]$$

$$VCp_2(defu) \rightleftarrows VCp_2 + defu \qquad (b)$$

$$K_b = [VCp_2][defu]/[VCp_2(defu)]$$

As the carbonylation of VCp_2, i.e. eq a in Scheme 2, is almost complete in toluene at 298 K,[9] it was more appropriate to study the reverse of reaction b, i.e. the addition of defu to VCp_2. It was then found (IR) that the addition of VCp_2 to defu is considerably shifted toward the formation of VCp_2(defu) with an equilibrium constant $1/K_b$ of 150 ± 11 at 298 K, corresponding to the equilibrium constant $K_b = (6.7 \pm 0.4) \times 10^{-3}$ for the release of defu from VCp_2(defu). Since $K_4 = K_aK_b$, the equilibrium constant K_a for the addition of CO to VCp_2, i.e. K_4/K_b, was evaluated to be about $(8.2 \pm 0.4) \times 10^3$.

Concluding Remarks

In this paper we have demonstrated that the reactions of VCp_2(CO) with olefins strongly depend on the substituents on the olefin. As a matter of fact, tcne (containing four cyano groups per carbon−carbon unsaturation) and fumaronitrile (two cyano groups per carbon−carbon unsaturation) completely displace ligated carbon monoxide from VCp_2(CO). In the case of acrylonitrile, i.e. on reducing the extent of electron withdrawal caused by the cyano group,[15a] the displacement of CO by the olefin corresponds to an equilibrium situation. No reaction was observed between VCp_2(CO) and unsubstituted olefins such as cyclooctene and norbornene, thus suggesting that the carbonyl complex is largely favored. This is certainly related to the strong π back-donating character of the CO ligand, as evidenced by the low value of $\tilde{\nu}_{CO}$, despite the positive oxidation state +II for the central metal atom.

The equilibrium constant for the substitution of complexed defu in VCp_2(defu) by CO is 55 ± 8 at 298.5 K (see eq 4). The reaction is not greatly affected by temperature; it is slightly exothermic, the corresponding enthalpy contribution being evaluated to be $\Delta H_4 = -2.4$ kcal/mol. The measurement of the equilibrium constant corresponding to the addition of defu to vanadocene ($1/K_b = 150 \pm 11$) has allowed us to evaluate the addition of CO to vanadocene, which, according to the experimental evidence reported in the literature,[9] is substantially quantitative. The relative affinity of CO and diethyl fumarate for VCp_2 in toluene solution may reasonably be assumed to correspond to the ratio of the corresponding equilibrium constants, i.e. $K_aK_b = 8.2 \times 10^3/150 = 55$.

It is of interest to compare the present data with those obtained in the reaction between AuCl(CO) and olefins.[4e] As mentioned earlier, AuCl(CO) is unreactive toward olefins containing electron-withdrawing substituents, whereas CO is displaced by cyclooctene and norbornene. It is interesting to point out that our earlier studies on the competitive CO/olefin equilibrium data for gold(I)[4e] are consistent with some theoretical estimates of the gold−CO[20] and gold−ethylene[21] bond energies in AuCl(CO) and $[Au(C_2H_4)]^+$, respectively. The values have been reported to be 43.5−52.6 kcal mol^{-1} (depending on the method of calculation) for Au(CO)Cl and 50.2 kcal mol^{-1} for $[Au(C_2H_4)]^+$. Related to this point are the available equilibrium data[22] on olefin complexes of 4d^2 niobium(III), 4d^8 palladium(II), and 5d^8 platinum-

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(II), showing that coordination of para-substituted styrenes is favored when the para position is occupied by electron-withdrawing groups in the case of niobium(III), whereas olefins containing electron-releasing substituents are preferred for palladium(II) and platinum(II). Similar to the case for $VCp_2(CO)$, $NbCp_2H(CO)$ exhibits[22g] a low carbonyl stretching vibration ($\tilde{\nu}_{CO}$ 1900 cm^{-1}), thus suggesting an elevated electron density at the metal. For silver(I),[23] a $4d^{10}$ system, most of the data are defined in aqueous systems, and they are not directly comparable with those available for gold(I).

In conclusion, this paper has established that the electron-rich vanadium(II) of $3d^3$ electronic configuration in VCp_2 has a different behavior with respect to gold(I), preferring CO to olefins with electron-withdrawing substituents and having no tendency to bind unsubstituted cyclic olefins. For carbonyl derivatives, the first qualitative indication of the behavior to be expected is given by the $\tilde{\nu}_{CO}$ values.

Experimental Section

General Considerations. Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods prior to use. Bis(cyclopentadienyl)vanadium(II), VCp_2, bis(cyclopentadienyl)carbonylvanadium(II), $VCp_2(CO)$, and bis(cyclopentadienyl)(diethyl fumarate)vanadium(II) were obtained according to literature procedures.[9,12,24] Tetracyanoethylene (tcne, Fluka), acrylonitrile, and fumaronitrile (fn, Fluka) were purified by sublimation or distillation prior to use. Diethylfumarate (defu, Fluka) and acrylonitrile were distilled under reduced pressure and stored at ca. −30 °C. IR spectra were recorded on a FT-1725X instrument on solutions (0.1 mm CaF_2 windows) or Nujol or polychlorotrifluoroethylene (PCTFE) mulls prepared with rigorous exclusion of moisture and air. The gas volumetric measurements were performed with the apparatus described by Calderazzo and Cotton.[17] The solubility of CO in toluene at different temperatures was obtained from literature data.[9]

Preparation of VCp_2(tcne) (1). A yellow solution of tcne (0.504 g, 3.93 mmol) in toluene (50 mL) was treated at room temperature with VCp_2 (0.706 g, 3.90 mmol), promptly giving a dark suspension. After 6 h of stirring at room temperature, the suspension was filtered, and the solid was washed with toluene and heptane and dried in vacuo at room temperature (1.098 g, 91% yield). Compound **1** is a dark brown solid sensitive to air. Anal. Found: C, 61.8; H, 3.6; N, 17.8. Calcd for $C_{16}H_{10}N_4V$: C, 62.1; H, 3.3; N, 18.1. IR (Nujol, cm^{-1}): 3109 w, 2216 w, 2173 m, 2154 m, 2012 vs, 1358 m-w, 843 m, 817 m.

The reaction of $VCp_2(CO)$ with an equimolar amount of tcne proceeds with vigorous and quantitative evolution of CO and formation of the same compound.

Preparation of VCp_2(fumaronitrile) (2). A solution of fumaronitrile (0.038 g, 0.49 mmol) in toluene (25 mL) was treated at room temperature with $VCp_2(CO)$ (0.098 g, 0.49 mmol). A brown solid formed with evolution of carbon monoxide within the time of mixing of the reagents. After 6 h of stirring at room temperature, a green solid was present. An IR spectrum of the solution showed the absence of absorptions attributable to carbonyl derivatives. The suspension was filtered and the solid was washed with toluene and heptane and dried in vacuo at room temperature, affording 0.094 g (73% yield) of **2** as a green-brown solid sensitive to air. Anal. Found: C, 65.2; H, 4.9; N, 11.2. Calcd for $C_{14}H_{12}N_2V$: C, 64.9; H, 4.7; N, 10.8. IR (Nujol, cm^{-1}): 3112 w, 2188 s, 1962 w, 1160 m, 1026 m, 1011 m, 824 m. The same compound was obtained from VCp_2 and fumaronitrile in toluene or THF.

The $VCp_2(CO)$/Acrylonitrile System by Gas Volumetry. In a thermostated system, a solution of acrylonitrile (0.1 mL, 1.52 mmol) in toluene (50 mL) and a thin-walled sealed glass container containing $VCp_2(CO)$ (0.319 g, 1.53 mmol) (acrylonitrile/V = 1) were introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric buret and saturated with CO at atmospheric pressure at 294.6 K. After breakage of the thin-walled container, gas evolution was observed up to a CO/V molar ratio of 0.014.

In a thermostated system, a thin-walled sealed glass vial containing VCp_2(acrylonitrile) (0.152 g, 0.65 mmol) was introduced into an Erlenmeyer flask equipped with a lateral stopcock together with toluene (50 mL). The system was connected to a gas volumetric buret and saturated with CO at atmospheric pressure at 294.6 K. By using the methods described above, gas evolution was observed up to a CO/V molar ratio of 0.835.

Reaction between $VCp_2(CO)$ and Diethyl Fumarate. Evolution of gas was observed when a solution of defu (0.1 g, 0.61 mmol) in toluene (10 mL) was treated at room temperature with $VCp_2(CO)$ (0.123 g, 0.61 mmol). The IR spectrum of the solution measured after 2 h showed absorptions at 1882, 1725, and 1678 cm^{-1} attributed to $VCp_2(CO)$ and uncoordinated and coordinated diethyl fumarate, respectively. After an additional 2 h, the spectrum did not show any significant change. These spectral features were also noted when VCp_2(diethyl fumarate) was exposed to an atmosphere of carbon monoxide in toluene solution. The reaction was repeated in a gas volumetric apparatus (T = 294.6 K) under the same experimental conditions, and evolution of CO up to the molar ratio CO/V = 0.09 was observed. A control experiment was performed by carbonylating VCp_2(diethyl fumarate) in a gas volumetric apparatus under the same experimental conditions as described above. Absorption of CO was observed up to a CO/V molar ratio of 0.92.

The $VCp_2(CO)/VCp_2$(defu) Equilibrium by Gas Volumetry. Starting from $VCp_2(CO)$. In a thermostated system, a solution of defu in toluene (50 mL) and a thin-walled sealed glass vial containing $VCp_2(CO)$ were introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric buret and saturated with CO at atmospheric pressure at the temperature of the experiment. The container was then broken by mechanical stirring, and the evolution of gas was measured at regular intervals of time. According to earlier work from these laboratories,[9] the molar concentration of CO in toluene is practically independent of temperature in the range used for the present experiments. The solubility at 298 K (7.5 × 10^{-3} M) has been used in the calculations. The temperature of the experiment, the starting molar concentations of $VCp_2(CO)$ and defu, and the measured $CO_{evolved}/V$ (CO/V) molar ratios at equilibrium, respectively, are reported:

$$T = 298.5\ \mathrm{K},\ [\mathrm{VCp_2(CO)}]_i = 1.96 \times 10^{-2};\quad [\mathrm{defu}]_i = 0.195;\ \mathrm{CO/V} = 0.31$$

$$T = 308.1\ \mathrm{K},\ [\mathrm{VCp_2(CO)}]_i = 2.52 \times 10^{-2};\quad [\mathrm{defu}]_i = 0.244;\ \mathrm{CO/V} = 0.36$$

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$$T = 317.7\ \text{K},\ [\text{VCp}_2(\text{CO})]_i = 2.10 \times 10^{-2};\quad [\text{defu}]_i = 0.208;\ \text{CO/V} = 0.34$$

$$T = 327.7\ \text{K},\ [\text{VCp}_2(\text{CO})]_i = 1.76 \times 10^{-2};\quad [\text{defu}]_i = 0.183;\ \text{CO/V} = 0.34$$

Each of the gas volumetric experiments was repeated at least three times, to obtain consistent CO/V molar ratios.

Starting from VCp_2(defu). A solution of defu in toluene (50 mL) and a thin-walled sealed glass container containing VCp_2(defu) were introduced into an Erlenmeyer flask equipped with a lateral stopcock. The system was connected to a gas volumetric buret and saturated with CO at atmospheric pressure at the temperature of the experiment. The container was then broken by mechanical stirring, and the absorption of gas was measured. The temperature of the experiment, the starting molar concentrations of VCp_2(defu) and defu, and the measured $CO_{absorbed}$/V molar ratios (CO/V) at equilibrium, respectively, are reported:

$$T = 298.5\ \text{K},\ [\text{VCp}_2(\text{defu})]_i = 1.24 \times 10^{-2};\quad [\text{defu}]_i = 0.122;\ \text{CO/V} = 0.76$$

$$T = 308.1\ \text{K},\ [\text{VCp}_2(\text{defu})]_i = 1.58 \times 10^{-2};\quad [\text{defu}]_i = 0.159;\ \text{CO/V} = 0.69$$

$$T = 317.7\ \text{K},\ [\text{VCp}_2(\text{defu})]_i = 1.32 \times 10^{-2};\quad [\text{defu}]_i = 0.134;\ \text{CO/V} = 0.69$$

$$T = 327.7\ \text{K},\ [\text{VCp}_2(\text{defu})]_i = 1.20 \times 10^{-2};\quad [\text{defu}]_i = 0.122;\ \text{CO/V} = 0.69$$

Each of the gas volumetric experiments was repeated at least three times, to obtain consistent CO/V molar ratios.

The VCp_2(defu)/VCp_2 Equilibrium by IR Spectroscopy. A 0.08 M solution of defu in toluene (10 mL) was treated at 298.5 K with VCp_2 (0.144 g, 0.8 mmol), giving a brown-green solution. After 15 h, the following concentrations (M) were obtained by measuring the intensity of the IR absorption at 1724 cm^{-1} due to uncoordinated defu (ϵ_{1724} of defu in toluene 12.7 $M^{-1}cm^{-1}$): $[\text{defu}]_{eq} = 0.02$; $[\text{VCp}_2]_{eq} = 0.02$; $[\text{VCp}_2(\text{defu})]_{eq} = 0.06$. Thus, the equilibrium constant K_b for reaction b of Scheme 2 was evaluated to be $(6.7 \pm 0.4) \times 10^{-3}$ at 298.5 K, corresponding to the equilibrium constant $1/K_b = 150 \pm 11$ for the formation of the defu complex.

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