Organometallics **1989**, *8*, 1598–1604

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Registry No. **1a**, 109031-61-0; **1b**, 120410-89-1; **1c**, 120410-90-4; **1d**, 120445-27-4; **1e**, 120410-91-5; **1f**, 120410-92-6; **1g**, 120410-93-7; **2a**, 27490-32-0; **2b**, 87996-30-3; **2c**, 66222-28-4; **2d**, 120385-24-2; **2e**, 120385-25-3; **2f**, 120385-26-4; **2g**, 120385-27-5; **3c**, 120410-94-8; **3d**, 120410-95-9; **3e**, 120410-96-0; Bu_3SnCH_2I, 66222-29-5; Bu_3SnCD_2I, 120385-28-6; Bu_3SnLi, 4226-01-1; MeOh, 67-56-1; $ClCH_2OCH_2Ph$, 3587-60-8; Cp_2ZrCl_2, 1291-32-3; *p*-methoxybenzyl alcohol, 105-13-5; (*S*)-(−)-*sec*-phenethyl alcohol, 1445-91-6; acetophenone, 98-86-2; 1-deuterio-*sec*-phenethyl alcohol, 3101-96-0; (±)-*sec*-phenethyl alcohol, 13323-81-4; phenethyl alcohol, 60-12-8; (*S*)-1-acetoxy-2-phenyl propane, 50373-50-7; (*R*)-1-acetoxy-2-phenyl propane, 73308-18-6.

Supplementary Material Available: A table listing final positional and thermal parameters (1 page); a listing of final observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Photochemistry of (η^5-Cyclopentadienyl)tetracarbonylvanadium in Frozen Gas Matrices at ca. 12 K. Infrared Spectroscopic Evidence for Species Arising from Carbon Monoxide Ejection and Ring Dechelation Processes

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Infrared spectroscopic evidence, including ^{13}CO labeling and energy-factored force-field fitting of terminal metal carbonyl stretching vibrations, is presented showing that irradiation of $V(\eta^5\text{-}C_5H_5)(CO)_4$ at high dilution in frozen gas matrices at ca. 12 K results in two types of reversible process. One process (Ar, CH_4) is ejection of CO to yield the species $V(\eta^5\text{-}C_5H_5)(CO)_n$ (n = 1–3) that may be related to the dissociative pathways proposed for thermal and photochemical substitution reactions in solution at 298 K. The second process (Ar, CH_4, N_2, and CO) is proposed to involve a change in the ring hapticity with the formation of $V(\eta^3\text{-}C_5H_5)(CO)_4$ and probably $V(\eta^3\text{-}C_5H_5)(CO)_5$ (CO matrices). The detection of these ring dechelation species suggests that the contribution of a S_N2 pathway to the solution substitution reactions should be reevaluated. In reactive and doped matrices (N_2, C_2H_4 doped CH_4) irradiation yielded $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$, $V(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_4)$, and *trans*-$V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$ species.

The photolability of $V(\eta^5\text{-}C_5H_5)(CO)_4$ has been employed in preparing a variety of $V(\eta^5\text{-}C_5H_5)(CO)_{4-m}L_m$ complexes by irradiating $V(\eta^5\text{-}C_5H_5)(CO)_4$ in the presence of L. In the case of monodentate ligands, e.g. L = diene,[1] PPh_3,[2–4] $P(n\text{-}Bu)_3$,[5] PH_3,[6] or EMe_2 (E = S, Te),[7] the products are monosubstituted complexes of the type $V(\eta^5\text{-}C_5H_5)(CO)_3L$. Photoreactions with bidentate phosphines (L-L), e.g. L-L = $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 4)[8] or $PhP(CH_2CH_2PPh_2)_2$,[9] gave disubstituted complexes of the type *cis*-$V(\eta^5\text{-}C_5H_5)(CO)_2(L\text{-}L)$. A bidentate amine ligand NN*, a Schiffs base formed by condensation of 2-formylpyridine and 1-amino-1-methyltoluene, also formed a disubstitution product, $V(\eta^5\text{-}C_5H_5)(CO)_2(NN^*)$, when irradiated with $V(\eta^5\text{-}C_5H_5)(CO)_4$ in tetrahydrofuran (THF).[10] Irradiation of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in the presence of acetylenes ($RC\equiv CR'$), e.g. R = H and R′ = H, *n*-Pr, *n*-Bu, or CMe_3[3] and R = R′ = Ph,[11–13] C_6F_5,[12] Me,[13] or $SiMe_3$,[13] has afforded the acetylene complexes $V(\eta^5\text{-}C_5H_5)(CO)_2(RC\equiv CR')$. The only bis(acetylene) complex is $V(\eta^5\text{-}C_5H_5)(CO)(PhC\equiv CPh)_2$ which was formed on treating $V(\eta^5\text{-}C_5H_5)(CO)_2(PhC\equiv CPh)$ with a further mole of $PhC\equiv CPh$. Interestingly, acetylenes can stabilize highly electron-deficient species, e.g. $V(\eta^5\text{-}C_5H_5)(CO)(PhC\equiv CPh)$[2] and $V(\eta^5\text{-}C_5H_5)(CO)(F_5C_6C\equiv CC_6F_5)$.[12]

Kinetic studies of the thermal substitution reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$ with a variety of phosphines and phosphites have suggested that the reactions proceed by dissociative paths in which loss of a CO ligand is the rate-determining step.[14] Although the quantum yield data for the photochemical reaction of $V(\eta^5\text{-}C_5H_5)(CO)_4$ with PPh_3 was consistent with an associative path, this was ruled out because it seemed unlikely that a sterically crowded 20-electron intermediate, $V(\eta^5\text{-}C_5H_5)(CO)_4(PPh_3)$, could be formed.[4] Instead, the photosubstitution reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$ have been proposed to involve dissociative

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loss of CO, i.e. eq 1–3 where the asterisk (*) denotes an excited-state species.

$$V(\eta^5\text{-}C_5H_5)(CO)_4 \xrightarrow{h\nu} V(\eta^5\text{-}C_5H_5)(CO)_4{}^* \quad (1)$$

$$V(\eta^5\text{-}C_5H_5)(CO)_4{}^* \rightarrow V(\eta^5\text{-}C_5H_5)(CO)_3 + CO \quad (2)$$

$$V(\eta^5\text{-}C_5H_5)(CO)_3 + PPh_3 \rightarrow V(\eta^5\text{-}C_5H_5)(CO)_3(PPh_3) \quad (3)$$

In the case of photoreactions carried out in THF, which is a coordinating solvent, the CO loss product is trapped as a solvate species before the THF is displaced by the entering ligand:

$$V(\eta^5\text{-}C_5H_5)(CO)_3 \xrightarrow{THF} V(\eta^5\text{-}C_5H_5)(CO)_3(THF) \quad (4)$$

$$V(\eta^5\text{-}C_5H_5)(CO)_3(THF) + L \rightarrow V(\eta^5\text{-}C_5H_5)(CO)_3L + THF \quad (5)$$

The fact that $V(\eta^5\text{-}C_5H_5)(CO)_3(THF)$ can actually be isolated[15] provides strong evidence for the dissociative path. Certainly the use of THF as a solvent affords the most general synthetic method.

Matrix-isolation studies[16] have been very successful in characterizing a variety of photochemically generated organometallic species[17,18] which have been proposed as reaction intermediates. We report here the photochemistry of $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated in frozen gas matrices at ca. 12 K, and we relate the results to the substitution reactions in solution at 298 K.

Experimental Section

The cryogenic equipment and vacuum system, matrix gases, infrared, and UV–visible spectrometers, and the medium-pressure Hg arc photolysis lamp have been described elsewhere.[19] The sample of $V(\eta^5\text{-}C_5H_5)(CO)_4$ was purchased from Strem Chemicals Inc and purified by sublimation (18 °C, 0.5 Torr) prior to use. Matrices containing $V(\eta^5\text{-}C_5H_5)(CO)_4$ were prepared by cocondensing the vapor of the complex, held in a glass finger, with a large excess of matrix gas from a bulb. The vapor of the complex was controlled by using a constant temperature bath (20 °C), and the flow of matrix gas was regulated by using a needle valve. The sample window was CaF_2 (BDH Ltd). The ^{13}CO-enriched sample of $V(\eta^5\text{-}C_5H_5)(^{12}CO)_{4-n}(^{13}CO)_n$ (n = 1–4) was prepared by a method analogous to that described previously,[19] cf the earlier method of enrichment involving ^{13}CO and $^{12}C^{18}O$ in hexane[20] and the more recent route for ^{13}CO via the $V(\eta^5\text{-}C_5H_5)(CO)_3(THF)$ complex.[21] Wavelength-selective photolyses were achieved by using the following Corning glass color filters (3 mm thick): filter A, $\lambda >$ 420 nm, CS 3-74; filter B, $320 < \lambda < 390$ nm, CS 7-60; and filter C, $\lambda >$ 520 nm, CS 3-70.

Results

The electronic spectrum of $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in a CH_4 matrix (1:2000–1:5000) at ca. 12 K (Figure 1a) is dominated by absorption bands in the UV region (λ_{max} = 280 and 364 nm) with a weak absorption in the blue region of the visible spectrum (λ_{max} = 410 nm). The long wavelength band could possibly be a d → d transition while those bands at higher energy are likely to be V → π*(CO) charge-transfer transitions.[22]

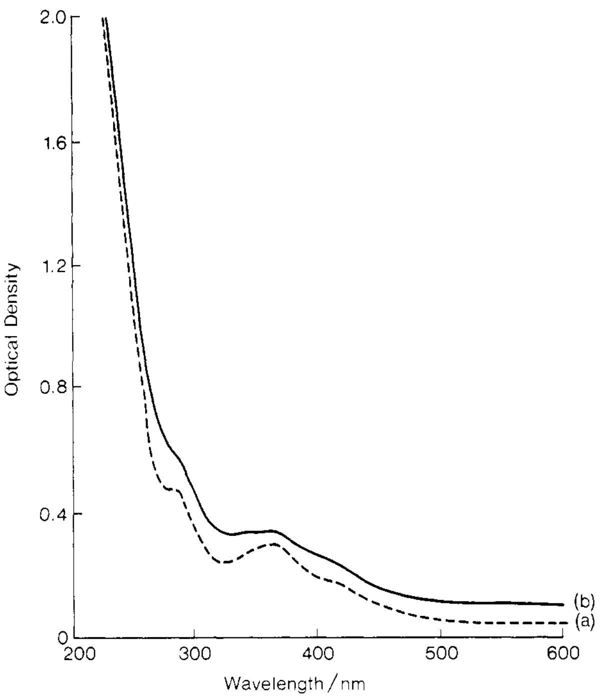

Figure 1. Electonic absorption spectra (Pye Unicam SP1800B) from an experiment with $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in a CH_4 matrix at ca. 12 K: (a) after deposition (b) after 5-min visible irradiation (filter A).

Photolysis of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in Ar and CH_4 Matrices. The infrared spectra from an experiment with $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in an Ar matrix at ca. 12 K, are shown in Figure 2. The spectrum on deposition (Figure 2a) shows matrix split terminal CO stretching bands at 2034.1 and 1936.2 cm^{-1} (Table I) expected for the A_1 and E modes, respectively, of a C_{4v} local symmetry $V(CO)_4$ fragment.[23-25] The appearance of the infrared inactive B_1 band at 1957.4 cm^{-1} is indicative of some deviation from strict C_{4v} local symmetry. A short period of visible irradiation (filter A, $\lambda >$ 420 nm) produced five new bands at 2138.0 ("free" CO), 2023.1, 1964.4, 1901.8, and 1866.6 cm^{-1} and a shoulder at ca. 1935 cm^{-1}. Further irradiation with UV light (Filter B, $320 < \lambda < 390$ nm) caused all the new bands to increase in intensity at the expense of the parent bands, and the shoulder band was resolved into a separate band at 1934.7 cm^{-1} (Figure 2c). On long wavelength irradiation (filter C, >520 nm) or annealing the matrix to ca. 35 K, a rapid intensity decrease was observed in the band of "free" CO and in the bands at 1964.4, 1901.8, and 1866.6 cm^{-1} with concomitant increases in intensity of the parent bands (parts d and e, respectively, of Figure 2). In contrast to this, the bands at 2023.1 and 1934.7 cm^{-1} increased in intensity on long wavelength irradiation and decreased in intensity on annealing. From the behavior (increase/decrease in intensity) of the product bands upon various photolysis conditions and annealing, it is possible to identify two different species (species **1**, 2023.1, 1934.7 cm^{-1}; species **2**, 1964.4, 1901.8, 1866.6 cm^{-1}). The high dilution used (ca. 1:2000–1:5000) and the reversibility of the reactions photochemically and thermally (annealing) rules out the

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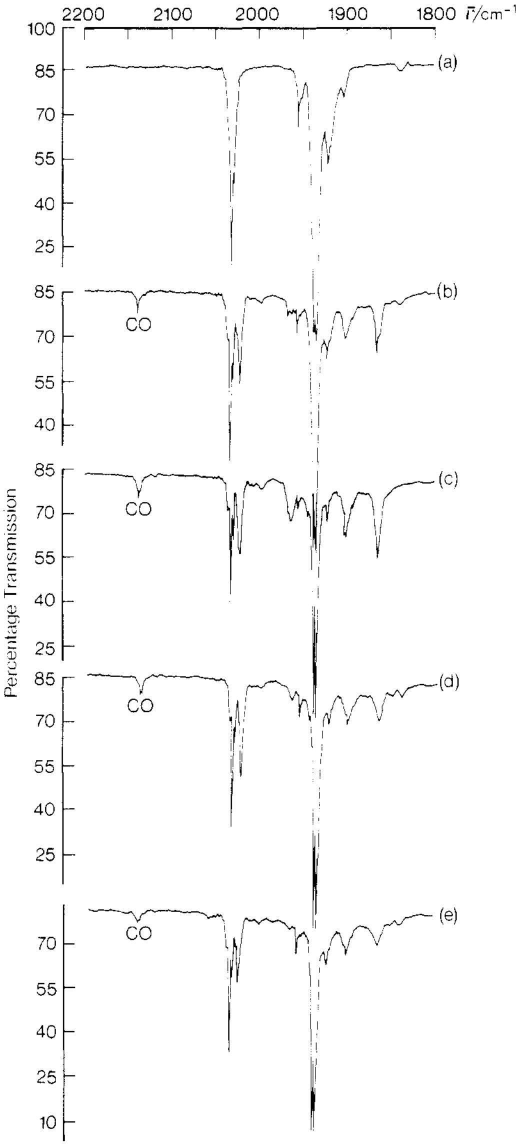

Figure 2. Infrared spectra (Nicolet FTIR 7199) from an experiment with $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in an Ar matrix at ca. 12 K: (a) after deposition, (b) after 15-min visible irradiation (filter A), (c) after 20-min UV irradiation (filter B), (d) after further 15-min visible irradiation (filter C), and (e) after annealing to ca. 35 K.

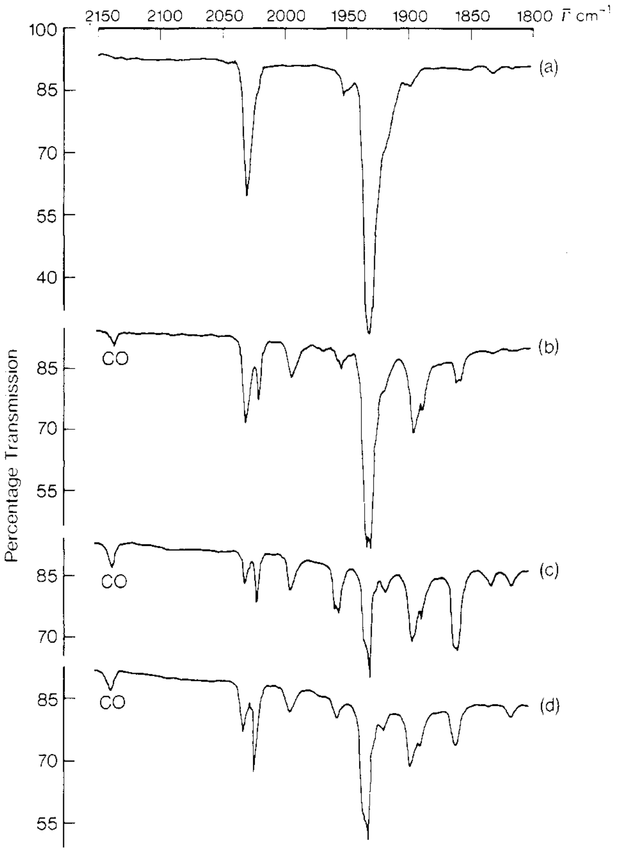

Figure 3. Infrared spectra (Nicolet FTIR 7199) from an experiment with $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in a CH_4 matrix at ca. 12 K: (a) after deposition, (b) after 5-min visible irradiation (filter A), (c) after 5-min UV irradiation (filter B), and (d) after further 10-min visible irradiation (filter C).

possibility of any polynuclear aggregates, e.g., $V_2(\eta^5\text{-}C_5H_5)_2(CO)_5$.[3,26] The fact that the formation of photochemically generated "free" CO is observed suggests ejection of CO from the parent complex has occurred. The most probable formulation for one product species is $V(\eta^5\text{-}C_5H_5)(CO)_3$. In most organometallic carbonyl complexes, formation of coordinatively unsaturated 16-electron species during decarbonylation processes results in band shifts of ca. 50 cm^{-1} to lower wavenumbers. Consequently, species **2** (ν_{CO} at 1964.4, 1901.8, and 1866.6 cm^{-1}) can probably be assigned as $V(\eta^5\text{-}C_5H_5)(CO)_3$ (see below). Interestingly the band positions of the $V(\eta^5\text{-}C_5H_5)(CO)_3$ fragment are comparable to those of the saturated vanadium tricarbonyl phosphine complexes $V(\eta^5\text{-}C_5H_5)(CO)_3(PH_3)$ (ν_{CO} at 1975, 1901, and 1876 cm^{-1} in hexane)[6] and $V(\eta^5\text{-}C_5H_5)(CO)_3(PPh_3)$ (ν_{CO} at 1960, 1885, and 1865 cm^{-1} in benzene).[4]

The band positions of species **1** are only ca. 10 cm^{-1} lower than those of the parent complex. The magnitude of downward wavenumber shift in this case is similar to those encountered for the proposed partial dechelation of a hydrocarbon ring coordinated to a metal; e.g., $Fe(\eta^4\text{-}C_4H_4)(CO)_3 \rightarrow Fe(\eta^2\text{-}C_4H_4)(CO)_3$ and $Fe(\eta^4\text{-}C_8H_8)(CO)_3 \rightarrow Fe(\eta^2\text{-}C_8H_8)(CO)_3$ dechelations resulted in 13 and 12 cm^{-1} downward shifts,[27,28] respectively. Taking into account the possible formation of $V(\eta^3\text{-}C_5H_5)(CO)_5$ in a CO matrix (see below), species **1** may tentatively be assigned as the coordinatively unsaturated ring slippage species $V(\eta^3\text{-}C_5H_5)(CO)_4$.[37]

The infrared spectrum of $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in a CH_4 matrix at ca. 12 K is similar to that in an Ar matrix (Figure 3a, Table I). A short period of visible irradiation (filter A) produced two further new bands at 1992.5 and 1893.9 cm^{-1} besides those due to "free" CO, **1** (ν_{CO} at 2019.9 and 1928.1 cm^{-1}) and **2** (ν_{CO} at 1953.5 and 1887.0 and a doublet centered at 1857 cm^{-1} (Figure 3b, Table I). No significant change in the electronic spectrum could be detected at this stage (Figure 1b).[38] Further irradiation with UV light (filter B) for a short period increased the intensity of bands attributed to $V(\eta^3\text{-}C_5H_5)(CO)_4$ (**1**) and $V(\eta^5\text{-}C_5H_5)(CO)_3$ (**2**) together with slight decreases in intensities of bands at 1992.5 and 1893.9 cm^{-1} (**3a**) and the production of three more new bands at 1915.1, 1830.2, and 1813.7 cm^{-1} (Figure 3c). On long wavelength irradiation (filter C) or annealing (not illustrated) all the new bands were found to decrease in in-

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Table I. Observed Infrared Positions (cm^{-1}) of Terminal CO Stretching Bands for $V(\eta^5\text{-}C_5H_5)(CO)_4$ and Its Photolysis Products Isolated at High Dilution in Various Gas Matrices at ca. 12 K

compd	Ar	CH_4	N_2	C_2H_4/ CH_4	CO
$V(\eta^5\text{-}C_5H_5)(CO)_4$	2034.1 2031.2 ^{a}	2030.2	2033.2	2026.1	2030.2
	$(1957.4)^{b}$	$(1952.1)^{b}$	$(1954.9)^{b}$	$(1946.1)^{b}$	$(1952.1)^{b}$
	1938.6 1936.2 1922.9 1905.7 ^{a}	1930.9	1938.4 1931.1 ^{a}	1922.8	1929.7
$V(\eta^3\text{-}C_5H_5)(CO)_4$	2023.1	2019.9	2023.0		2021.4
	1934.7	1928.1	*c*		*c*
$V(\eta^5\text{-}C_5H_5)(CO)_3$	1964.4	1953.5		1952.3	
	1901.8	1887.0		1884.3	
	1866.6	1858.9 1856.2 ^{a}		*c*	
$V(\eta^5\text{-}C_5H_5)(CO)_2{}^{d}$		1992.5			
		1893.9			
$V(\eta^5\text{-}C_5H_5)(CO)_2{}^{e}$		1915.8			
		1813.7			
$V(\eta^5\text{-}C_5H_5)(CO)$		1830.2			
$V(\eta^5\text{-}C_5H_5)(CO)_3\text{-}(N_2)$			1995.6		
			1911.9		
			1875.1		
			2210.3^{f}		
$V(\eta^5\text{-}C_5H_5)(CO)_3\text{-}(C_2H_4)$				1967.4	
				c	
				1871.1	
$V(\eta^5\text{-}C_5H_5)(CO)_2\text{-}(C_2H_4)_2$				1888.9	
				1804.6	
$V(\eta^3\text{-}C_5H_5)(CO)_5$					2055.5
					1982.0
					1945.6

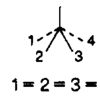
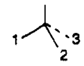
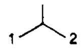
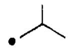
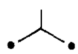
[a] Matrix splitting. [b] IR inactive band. [c] Obscured by overlapping band of another photoproduct. [d] Planar geometry. [e] Pyramidal geometry. [f] ν(NN).

tensity except the bands attributed to $V(\eta^3\text{-}C_5H_5)(CO)_4$ (1) and the parent bands which increased significantly (Figure 3d). The extra five bands observed in CH_4 matrices, i.e. bands at 1992.5, 1915.8, 1893.9, 1830.2, and 1813.7 cm^{-1}, could possibly be due to fragments derived from further decarbonylation of $V(\eta^5\text{-}C_5H_5)(CO)_3$. By comparison with the band positions of the saturated vanadium dicarbonyl complexes $V(\eta^5\text{-}C_5H_5)(CO)_2(HC{\equiv}CR)$ (R = H, ν_{CO} = 1996, 1925 cm^{-1}; R = *n*-Bu, ν_{CO} = 1990, 1910 cm^{-1}; R = CMe_3, ν_{CO} = 1994, 1920 cm^{-1}),[2] and the vanadium monocarbonyl complex $V(\eta^5\text{-}C_5H_5)(CO)(PPh_3)PhC{\equiv}CPh$ (ν_{CO} = 1825 cm^{-1}),[2] the bands at 1992.5 and 1893.9 cm^{-1} may tentatively be assigned to a $V(\eta^5\text{-}C_5H_5)(CO)_2$ species (**3a**) and the band at 1830.2 cm^{-1} to a $V(\eta^5\text{-}C_5H_5)(CO)$ fragment (Table I). The other band pair at 1915.8 and 1813.7 cm^{-1} may also be assigned tentatively to another type of dicarbonyl species (**3b**, see Discussion).

In order to ascertain the numbers of CO ligand in the photoproducts and to further identify the fragments, ^{13}CO isotopic labeling experiments and energy-factored force-field calculations were carried out.

Photolysis of $V(\eta^5\text{-}C_5H_5)(^{12}CO)_{4-n}(^{13}CO)_n$ (*n* = 0–4) Complexes in a CH_4 Matrix. The infrared spectrum of ^{13}CO-enriched $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in a CH_4 matrix at ca. 12 K showed mainly the bands of $V(\eta^5\text{-}C_5H_5)(CO)_3(^{13}CO)$ and *cis*- and *trans*-$V(\eta^5\text{-}C_5H_5)(CO)_2(^{13}CO)_2$.[39] The matrices were then irradiated with UV light for a similar period of time to that used above. Photoproducts and their ^{13}CO-enriched counterparts were obtained, and the mixed $^{12}CO/^{13}CO$ band positions were subjected to an energy-factored force-field fitting procedure.[29,30] The satisfactory agreement of the observed and

Table II. Observed and Calculated[a] Band Positions (cm^{-1}) of Terminal CO Stretching Bands for ^{13}CO-Enriched $V(\eta^5\text{-}C_5H_5)(CO)_4$ and Its Photolysis Products Isolated at High Dilution in CH_4 Matrices at ca. 12 K

compd	^{13}CO position (·)	ν_{CO}	obsd	calcd
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_4$		A_1	2030.1	2029.7
C_{4v}		B_2	1951.0^{b}	1949.5
	1 = 2 = 3 = 4	E	1930.5	1930.8
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_3(^{13}CO)$		A′	2021.8	2021.5
C_s		A′	1944.4	1945.0
		A″	1930.5	1930.8
		A′	1898.2	1899.9
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)_2$		A′	2011.7	2011.8
C_s		A′	1941.6	1942.1
		A″	1904.7	1904.6
		A′	*c*	1895.1
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)_2$		A_1	2012.5	2012.9
C_{2v}		A_1	1930.5	1930.8
		B_1	*c*	1922.1
		B_2	1888.1	1887.9
$V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_3$		A′	2000.7	2000.8
C_s		A′	1925.2	1924.3
		A′	1898.2	1897.1
		A″	1888.1	1887.9
$V(\eta^5\text{-}C_5H_5)(^{13}CO)_4$		A_1	1984.0	1984.5
C_{4v}		B_2	*b*, *c*	1906.2
		E	1888.1	1887.9
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_3$		A′	1953.3	1952.9
C_s		A′	1895.7	1894.7
	1 ≠ 2 = 3	A″	1856.8	1856.7
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)$		A′	1932.4	1933.0
C_s		A′	1871.1	1871.6
		A″	1856.8	1856.7
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)$		A	1946.7	1947.6
C_1		A	1887.0	1886.2
		A	*c*	1828.6
$V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_2$		A	*c*	1922.2
C_1		A	*c*	1869.2
		A	*c*	1828.0
$V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_2$		A′	*c*	1942.8
C_s		A′	*c*	1862.2
		A″	1815.6	1815.5
$V(\eta^5\text{-}C_5H_5)(^{13}CO)_3$		A′	1909.1	1909.5
C_s		A′	1851.8	1852.6
		A″	1815.6	1815.5
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_2{}^{d}$		A_1	1992.3	1992.9
$C_{2v}{}^{e}$	1 = 2	B_1	1895.7	1896.6
$V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)^{d}$		A	1976.0	1975.4
$C_1{}^{e}$		A	1871.7	1870.8
$V(\eta^5\text{-}C_5H_5)(^{13}CO)_2{}^{d}$		A_1	*c*	1948.6
$C_{2v}{}^{e}$		B_1	*c*	1854.2
$V(\eta^5\text{-}C_5H_5)(^{12}CO)_2{}^{f}$		A′	1914.3	1914.2
$C_s{}^{e}$	1 = 2	A″	1813.1	1813.2
$V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)^{f}$		A	1896.7	1897.1
$C_1{}^{e}$		A	1788.2	1788.9
$V(\eta^5\text{-}C_5H_5)(^{13}CO)_2{}^{f}$		A′	1871.7	1871.7
$C_s{}^{e}$		A″	1772.8	1771.9
$V(\eta^5\text{-}C_5H_5)(^{12}CO)$			1831.3	1830.0
$V(\eta^5\text{-}C_5H_5)(^{13}CO)$			1789.8	1789.2

[a] Refined energy-factored force-field constants (N m^{-1}) are as follows: $V(\eta^5\text{-}C_5H_5)(CO)_4$, $K = 1553.0$, $k_{12} = 32.2$, $k_{13} = 46.9$, cf. ref 20, $K = 1556.9$, $k_{12} = 27.9$, $k_{13} = 48.8$ ($^{12}C^{18}O$ data), and ref 24, $K = 1556$, $k_{12} = 31$, $k_{13} = 48$; $V(\eta^5\text{-}C_5H_5)(CO)_3$, $K_1 = 1508.1$, $K_2 = K_3 = 1437.9$, $k_{12} = k_{13} = 30.7$, $k_{23} = 45.1$; $V(\eta^5\text{-}C_5H_5)(CO)_2{}^{d}$ $K = 1528.9$, $k_i = 75.7$; $V(\eta^5\text{-}C_5H_5)(CO)_2{}^{f}$ $K = 1404.3$, $k_i = 76.1$; $V(\eta^5\text{-}C_5H_5)(CO)$, $K = 1354.3$. [b] Inactive. [c] Band predicted here obscured by another band. [d] *Planar* geometry. [e] Local symmetry for $V(CO)_2$ fragment. [f] *Pyramidal* geometry.

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(29) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

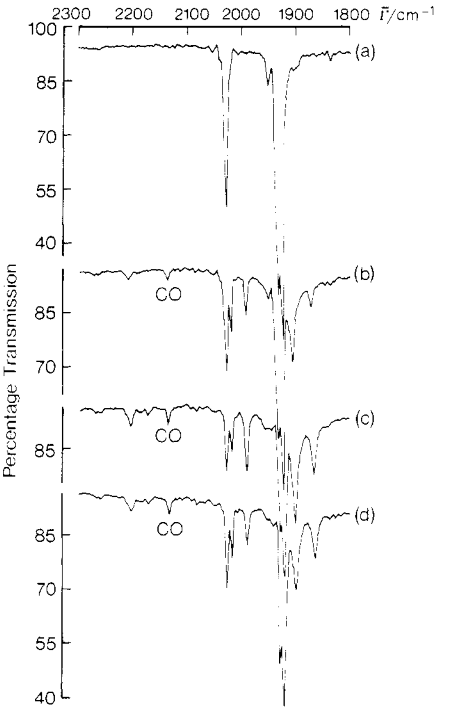

Figure 4. Infrared spectra (Nicolet FTIR 7199) from an experiment with V(η^5-C_5H_5)(CO)$_4$ isolated at high dilution in a N_2 matrix at ca. 12 K: (a) after deposition, (b) after 3-min visible irradiation (filter A), (c) after 2-min UV irradiation (filter B), and (d) after further 15-min visible irradiation (filter C).

calculated band positions (Table II) for the parent complex and its photolysis products confirms the C_{4v} local symmetry of the V(CO)$_4$ fragment of the parent molecule, the assignment of V(η^5-C_5H_5)(CO)$_3$ (**2**), and the existence of two types of dicarbonyl species V(η^5-C_5H_5)(CO)$_2$ (**3a**,**b**).[40] The computed force constants for V(η^5-C_5H_5)(CO)$_4$ in matrices (K = 1553.0, k_{12} = 32.3, k_{13} = 46.9 N m^{-1}) are very close to those calculated for cyclohexane solutions (K = 1556, k_{12} = 31, k_{13} = 48 N m^{-1}).[24]

Photolysis of V(η^5-C_5H_5)(CO)$_4$ in a N_2 Matrix. The infrared spectrum of V(η^5-C_5H_5)(CO)$_4$ isolated at high dilution in a N_2 matrix at ca. 12 K is very similar to those in Ar and CH_4 matrices (Figure 4a, Table I). A short period of visible irradiation (filter A) resulted in the appearance of six new bands at 2210.3, 2138.0 ("free" CO), 2023.0, 1995.6, 1911.9, and 1875.1 cm^{-1} at the expense of parent bands (Figure 4b). Ultraviolet irradiation (filter B) caused the new bands to gain intensity except the 2023.0 cm^{-1} band and the parent bands which showed reductions in intensities (Figure 4c). On further long wavelength irradiation (filter C) the opposite occurred; i.e. the parent bands together with the band at 2023.0 cm^{-1} regained intensity while the bands at 2210.3, 2138.0 ("free" CO), 1995.6, 1911.9, and 1875.1 cm^{-1} decreased slightly in intensity (Figure 4d). By analogy with the observations in Ar and CH_4 matrices, the band at 2023.0 cm^{-1} and another band obscured by the parent band at 1931.1 cm^{-1} can be assigned to V(η^3-C_5H_5)(CO)$_4$ (**1**). The fact that "free" CO was seen suggests that replacement of CO by an isoelectronic N_2 ligand has also occurred with the formation of a dinitrogen complex. Since the relative band intensities remained constant under various photolysis conditions, the photoproduct bands belong to a single new mononuclear species. The presence of three CO stretching bands (1995.6, 1911.9, and 1875.1 cm^{-1}) and single NN stretching (2210.3 cm^{-1}) suggests that the photoproduct must be V(η^5-C_5H_5)(CO)$_3$(N_2) (Table I). Surprisingly, further substitution of CO by N_2 to give the species V(η^5-C_5H_5)(CO)$_{4-m}$(N_2)$_m$ (m = 2, 3, or 4) and V(η^3-C_5H_5)(CO)$_4$(N_2) was not observed.

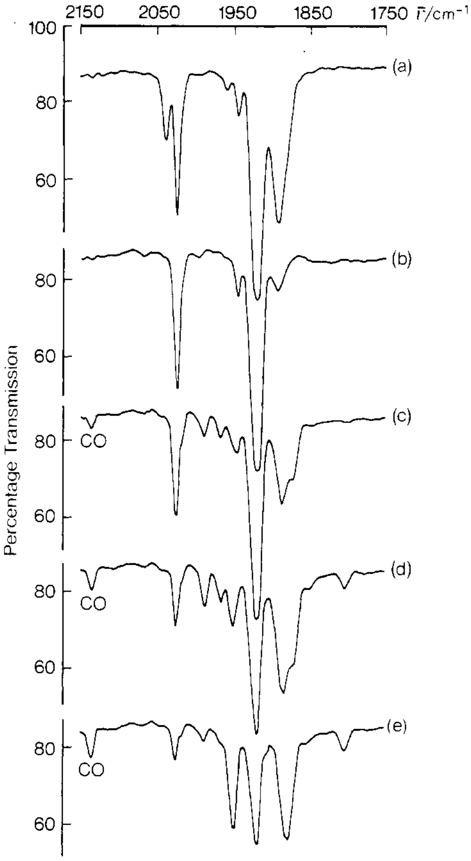

Figure 5. Infrared spectra (Nicolet FTIR 7199) from an experiment with V(η^5-C_5H_5)(CO)$_4$ isolated at high dilution in a C_2H_4 doped (25%) CH_4 matrix at ca. 12 K: (a) after deposition, (b) as (a) but with C_2H_4 bands subtracted out, (c) after 5-min visible irradiation (filter A), (d) after 5-min UV irradiation, and (e) after further 10-min visible irradiation (filter C). Bands due to C_2H_4 were also subtracted out from spectra c, d, and e.

Photolysis of V(η^5-C_5H_5)(CO)$_4$ in C_2H_4-Doped (25%) CH_4 Matrices. The infrared spectrum of V(η^5-C_5H_5)(CO)$_4$ isolated at high dilution in C_2H_4 doped (25%) CH_4 matrices at ca. 12 K is shown in Figure 5a. On removal of the C_2H_4 matrix bands by computer subtraction, the spectrum is similar to those in Ar, CH_4, and N_2 matrices (Figure 5b, Table I). A period of visible irradiation (filter A) led to the gradual appearance of seven new bands at 2138.0 ("free" CO), 1988.9, 1967.4, 1952.3, 1884.3, 1871.1, and 1804.6 cm^{-1} (Figure 5c). Further UV irradiation (filter B) caused all the new bands to increase in intensity at the expense of the parent bands (Figure 5d). Continued irradiation with visible light (filter A) resulted in reductions in intensities of the bands at 1988.9 and 1804.6 cm^{-1}, and the disappearance of bands at 1967.4 and 1871.1 cm^{-1}, with further increases in intensities of bands at 1952.3 and 1884.3 cm^{-1} (Figure 5e). From the behavior of the new product bands (increasing/decreasing in intensity) upon irradiation it is apparent that several product species are present, i.e. species X (1952.3, 1884.3 cm^{-1}), species Y (1967.4, 1871.1 cm^{-1}), and species Z (1988.9, 1804.6 cm^{-1}). The detection of "free" CO is indicative of decarbonylation and that substitution of CO by C_2H_4 has probably occurred in the photoreaction in the matrix. By analogy with the observations in Ar and CH_4 matrices species X can be confidently assigned to a naked tricarbonyl species, V-

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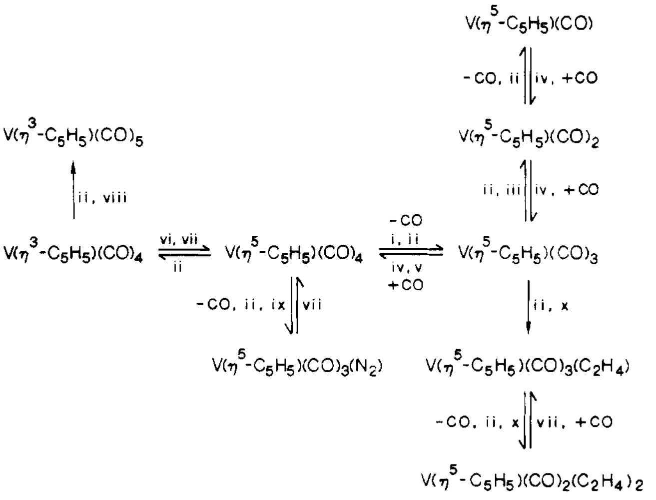
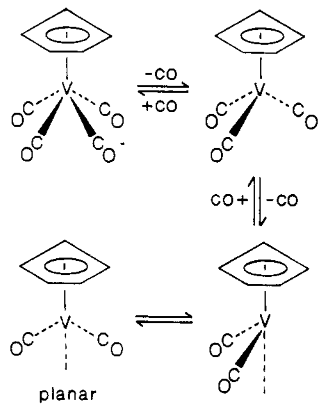
(30) Taylor, D. J. Ph.D. Thesis, University of Southampton, 1981.

Scheme I[a]



[a] i, Ar, CH_4, or C_2H_4-doped CH_4; ii, UV irradiation (filter B); iii, CH_4; iv, visible irradiation (filter C); v, annealing; vi, Ar, CH_4, N_2, or CO; vii, visible irradiation (filter A); viii, CO; ix, N_2; x, C_2H_4 doped CH_4.

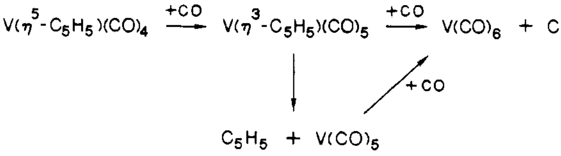
Scheme II



planar **3a** pyramidal **3b**

$(\eta^5\text{-}C_5H_5)(CO)_3$ (**2**), where the third band is obscured by one of the other product bands. By comparison with infrared data from solution studies, e.g. $V(\eta^5\text{-}C_5H_5)(CO)_3(PPh_3)$ (ν_{CO} at 1960, 1885, 1865 cm^{-1}),[4] species Y and Z can probably be assigned as $V(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_4)$ (ν_{CO} = 1967.4 and 1871.1 cm^{-1}) and $V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$ (ν_{CO} = 1988.9 and 1804.6 cm^{-1}), respectively (Table I).

Photolysis of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in a CO Matrix. The infrared spectrum of $V(\eta^5\text{-}C_5H_5)(CO)_4$ isolated at high dilution in a CO matrix at ca. 12 K is similar to that in Ar,CH_4,N_2, and C_2H_4-doped CH_4 matrices (Table I). A period of visible light photolysis (filter A) caused a band attributable to $V(\eta^3\text{-}C_5H_5)(CO)_4$, a broad band at ca. 1990 cm^{-1}, and a medium intensity band at 1894.4 cm^{-1} to begin to appear. Further UV irradiation (filter B) resulted in the broad band at ca. 1990 cm^{-1} being resolved into two bands at 1992.6 and 1982.0 cm^{-1}, the band at 1894.4 cm^{-1} increasing in intensity, and additional bands appearing at 2055.5 an 1945.6 cm^{-1} (shoulder band). On further long wavelength photolysis (filter C) the bands at 1992.6 and 1894.4 cm^{-1} disappeared. The appearance of the bands at 2055.5, 1982.0, and 1945.6 cm^{-1} at higher wavenumbers relative to the parent complex absorptions is analogous to the shift of product bands to higher wavenumbers when $Co(\eta^5\text{-}C_5H_5)(CO)_2$ was irradiated in a CO matrix.[31] In this case the product was assigned as $Co(\eta^3\text{-}C_5H_5)(CO)_3$, i.e., a shift to higher wavenumbers of terminal CO stretching bands may be associated with an increase in the number of bound CO ligands. Consequently, and taking into account the band positions of $V(\eta^3\text{-}C_5H_5)(CO)_4$ (ν_{CO} at ca. 2020 and 1930 cm^{-1}), it seems plausible to attribute the bands at 2055.5, 1982.0, and 1945.6 cm^{-1} to $V(\eta^3\text{-}C_5H_5)(CO)_5$. Surprisingly, the other product bands at 1992.6 and 1894.4 cm^{-1} do not correspond with either $V(CO)_6$ (ν_{CO} = doublet at 1976 and 1974 cm^{-1})[32] or $V(CO)_5$ (ν_{CO} = 1952 and 1943 cm^{-1}),[33] which are the expected photo-decomposition products of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in CO matrices (eq 6).[41]



(6)

Discussion

The photochemical reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in frozen gas matrices at ca. 12 K are summarized in Scheme I.

Irradiation with high-energy radiation (UV) in Ar and CH_4 matrices primarily resulted in ejection of CO ligands and the formation of reactive coordinatively unsaturated species $V(\eta^5\text{-}C_5H_5)(CO)_n$ (n = 1–3) where n has been established by ^{13}CO labeling. The observation of two $V(\eta^5\text{-}C_5H_5)(CO)_2$ species is significant in relation to molecular orbital calculations of the geometries of coordinatively unsaturated fragments.[25,34] In the case of the 16-electron species $Mn(\eta^5\text{-}C_5H_5)(CO)_2$ the *pyramidal* geometry was preferred over a *planar* geometry.[34] From a consideration of OC–M–CO (θ) bond angles in the first-row transition-metal $M(\eta^5\text{-}C_5H_5)(CO)_2$ species (M = Co, 18-electron complex, $\theta = 96°$ (solution)[35] and $\theta = 94°$ (CO matrix);[31] M = Mn, 16-electron complex, θ = 99 and 101° (Ar and CH_4 matrices)[36]), it should be possible to assign structures for the two $V(\eta^5\text{-}C_5H_5)(CO)_2$ species. Using the relative intensities of the terminal CO stretching bands, it was possible to calculate CO–V–CO bond angles of 77° (**3b**, ν_{CO} = 1915.8 and 1813.7 cm^{-1}) and 114° (**3a**, ν_{CO} = 1992.5 and

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(31) Crichton, O.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1980**, 167.

(32) Ford, T. A.; Hüber, H.; Klotzbücher, W.; Kündig, C. P.; Moskovits, M.; Ozin, G. A. *Inorg. Chem.* **1976**, *15*, 1666.

(33) Hanlan, L.; Hüber, H.; Ozin, G. A. *Inorg. Chem.* **1976**, *15*, 2592.

(34) Hoffman, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(35) Dalton, J.; Paul, I.; Stone, F. G. A. *J. Am. Chem. Soc.* **1974**, *96*, 4998.

(36) Fitzpatrick, N. J.; Rest, A. J.; Taylor, D. J. *J. Chem. Soc., Dalton Trans.* **1979**, 351.

(37) Infrared spectra showed very weak bands in other regions, e.g. $\nu_{M\text{-ring}}$, but little or no structural information has been definitely established for bands in these regions even for stable molecules.

(38) Electronic spectra invariably show broad structureless bands such that, without subtraction and first and second derivative plots (not available here), it is very difficult to locate new bands produced for species in low abundances.

(39) It was disappointing that ref 20 delineated data only for $^{12}C^{18}O$-enriched species when spectra for $^{13}C^{16}O$- and $^{12}C^{18}O$-enriched species were obtained.

(40) It was not possible to make an assignment for $V(\eta^3\text{-}C_5H_5)(CO)_4$ because the bands of this species are close to those of $V(\eta^5\text{-}C_5H_5)(CO)_4$ so that the $^{12}CO/^{13}CO$ patterns are impossibly overlapped.

(41) At this moment there is no satisfactory explanation for the bands at 1992.6 and 1894.4 cm^{-1}, but it is hoped that future work on $V(\eta^5\text{-}C_5Me_5)(CO)_4$ may provide some clues.

(42) Bond angle calculated from relative intensity using standard expressions $(I_{asym}/I_{sym}) = \tan^2(\theta/2)$. The ratio gives the angle between the CO oscillating dipole, which may or may not coincide with the CO band direction vectors.[29]

1893.9 cm^{-1}).[42] The small value of θ in the former case (**3b**) is what would be expected for a *pyramidal* geometry, with perhaps CH_4 filling the "vacant site", while the larger value in the second case (**3a**) indicates a planar geometry (Scheme II). The reactivities of the coordinatively unsaturated species were demonstrated by their recombination with ejected CO and with other reactants doped into the matrices, e.g. $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$ and $V(\eta^5\text{-}C_5H_5)(CO)_{4-n}(C_2H_4)_n$ ($n = 1, 2$). Calculations of the OC–V–CO angle (110°) and the interaction force constant (62.9 N m^{-1}) and comparison with related data ($k_{12} = 32.2$ and $k_{13} = 46.9$ N m^{-1}) for $V(\eta^5\text{-}C_5H_5)(CO)_4$ suggest that the bis(ethylene) species exists as the trans isomer, i.e. *trans*-$V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$. Although kinetic studies[14] and quantum yield measurements[4] favored dissociative paths for the thermal and photochemical substitution reactions of $V(\eta^5\text{-}C_5H_5)(CO)_4$, an associative pathway could not be ruled out. The possibility that a C_5H_5 could change its hapticity, e.g. $\eta^5 \rightleftharpoons \eta^3$ (ring slippage or partial dechelation), provides a feasible pathway for associative mechanisms in metal–cyclopentadienyl complexes. Such a hapticity change has been suggested for $Co(\eta^5\text{-}C_5H_5)(CO)_2$ in a CO matrix.[31] It is proposed, therefore, that the species formed on long wavelength photolysis of $V(\eta^5\text{-}C_5H_5)(CO)_4$ in all matrices (Ar, CH_4, N_2, CO) is the η^3-C_5H_5 species $V(\eta^3\text{-}C_5H_5)(CO)_4$ and that in a CO matrix this species may add a further CO ligand to give $V(\eta^3\text{-}C_5H_5)(CO)_5$ (18-electron species) or $V(\eta^1\text{-}C_5H_5)(CO)_5$ (16-electron species) depending on the electronic requirements for a filled shell versus steric crowding. The evidence in favor of ring-slippage η^3-C_5H_5 species suggests that the possible contribution of S_N2 pathways in solution thermal and photochemical reactions should be reevaluated for $V(\eta^5\text{-}C_5H_5)(CO)_4$.

Acknowledgment. We thank the Universiti Teknologi Malaysia for support (to R.B.H.) and the SERC for a grant (to A.J.R.).

Registry No. $V(\eta^5\text{-}C_5H_5)(CO)_4$, 12108-04-2; $V(\eta^3\text{-}C_5H_5)(CO)_4$, 120610-57-3; $V(\eta^5\text{k-}C_5H_5)(CO)_3$, 120610-58-4; $V(\eta^5\text{-}C_5H_5)(CO)_2$, 120610-59-5; $V(\eta^5\text{-}C_5H_5)(CO)$, 120610-60-8; $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$, 120610-61-9; $V(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_4)$, 120610-62-0; $V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$, 120610-63-1; $V(\eta\text{-}C_5H_5)(CO)_5$, 120636-93-3; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_3(^{13}CO)$, 99629-80-8; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)_2$ (isomer 1), 120610-64-2; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)_2$ (isomer 2), 120707-79-1; $V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_3$, 120610-65-3; $V(\eta^5\text{-}C_5H_5)(^{13}CO)_4$, 120610-66-4; $V(\eta^5\text{-}C_5H_5)(^{12}CO)_2(^{13}CO)$, 120610-67-5; $V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)_2$, 120610-68-6; $V(\eta^5\text{-}C_5H_5)(^{13}CO)_3$, 120610-69-7; $V(\eta^5\text{-}C_5H_5)(^{12}CO)(^{13}CO)$, 120610-70-0; $V(\eta^5\text{-}C_5H_5)(^{13}CO)_2$, 120610-71-1; $V(\eta^5\text{-}C_5H_5)(^{13}CO)$, 120610-72-2.

(Methylenephosphoranyl)methyl, Phosphinylmethyl, and Phosphinothioylmethyl Complexes of Tantalum

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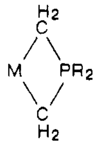
Received July 25, 1988

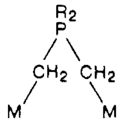
The reactions of lithium salts of the anionic ylides $(CH_2)_2PRR'$ ($R = R' = Me$; $R = Me$, $R' = Ph$; $R = R' = Ph$) and pseudoylides $(CH_2)P(X)Ph_2$ ($X = O, S$) with tetrachloro(pentamethylcyclopentadienyl)tantalum(V) give several new derivatives, $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)_2PRR'$ and $Ta(\eta^5\text{-}C_5Me_5)Cl_3(CH_2)P(X)Ph_2$. The structural characterization of these compounds is based on ^1H and ^{31}P NMR spectroscopic data.

Introduction

We recently reported[1] the isolation of the first neutral (alkylidenephosphorane)tantalum complexes. Since a number of isomeric forms are possible in much of the ylide chemistry, we sought to explore the extent that tantalum would assume the different known structures. In particular, the difunctionalized anionic ylides of the type $[(CH_2)_2PR_2]^-$ can function as terminal, chelate, or bridging ligands to give the isomeric structures A–D.



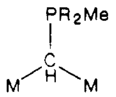
A



B

$M{=}CHPR_2Me$

C



D

Complexes containing alternatively one of these structures have been reported for different metals,[2] and in some cases[3] equilibria between them have been found.

We observed that reactions of neutral (alkylidenephosphorane)tantalum complexes with an excess of the phosphorus ylide did not take place at room temperature and not transylidation but formation of complicated unresolvable mixtures was obtained on heating.

An alternative method to prepare this type of complexes with phosphonium bis(ylide) anions is the reaction of the halide with lithium phosphoylide.[4] Here we report the results obtained in these reactions and the structural study of the products as well as the preparation and characterization of complexes containing the pseudoylide ligand $[(CH_2)P(X)Ph_2]^-$ ($X = O, S$).[5]

Results and Discussion

The reaction represented in eq 1 was performed by adding n-hexane to an equimolar mixture of the solid

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