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Spectroscopy and Photochemistry of the Tetranorbornyl Complexes of Titanium and Chromium

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Electronic spectra of the title compounds are reported. Ultraviolet band systems in both complexes are assigned as due to ligand-to-metal charge-transfer (LMCT) transitions, while visible absorptions in the chromium complex are assigned as due to ligand field (LF) excitations. The LMCT excited states in both complexes yield homolytic metal norbornyl bond cleavage with quantum yields of 0.03–0.05, while the quantum yields for visible irradiation of the chromium complex drop precipitously with increasing wavelength, indicating that the LF excited states do not yield net photochemistry. Quantum yields for production of organic photoproducts from the chromium complex are reported for hexane and CCl_4 solutions, and likely mechanisms are discussed. A new, higher yield synthesis of 1,1′-binorbornyl is also reported.

Metal alkyl complexes have become important over the last 15 years as precursors of and models for catalysts involved in transformations of hydrocarbons. Most of this research has involved the thermal chemistry of metal–carbon bonds,[1] but the photochemistry of these linkages has also been of increasing interest. Alkyl radicals have been identified as primary photoproducts in the photocleavage of some metal–alkyl bonds,[2] but in most cases little else is known about the primary photoprocess.

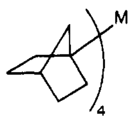
In most of the complexes studied to date, there are also other ligands present in the coordination sphere. In many cases these other ligands severely perturb or even dominate the electronic absorption spectrum; for example, alkylcobalt(III) corrinoids have a spectrum dominated by intense absorptions due to ligand-localized $\pi \rightarrow \pi^*$ transitions.[3] Complexes with aromatic phosphines or cyclopentadienyl groups have intense aromatic absorptions in the ultraviolet region of the spectrum. The situation becomes even more difficult when these other ligands are more labile than the alkyl group. This has been a problem in the study of metal carbonyl alkyl systems. Proposals that the observed photochemistry was due to photoinduced metal alkyl cleavage[4] have been modified since the realization that the dissociation of carbon monoxide is an important primary photoprocess.[5]

In designing an investigation of the excited-state structure and reactivity of metal alkyls, the highly symmetric homoleptic[6] alkyls are attractive. In addition, reports that tetraalkylmetal complexes possess photosensitive metal–alkyl linkages are encouraging. Photoassisted polymerizations of alkenes using Ti, Zr, and Hf tetrabenzyls[7] and tetraneopentyltitanium[8] are apparently catalyzed by reduced species formed by homolytic metal–alkyl cleavage. Long-term photolyses yield net metal reduction; e.g., $Cr(CO)_6$ is produced in the photolysis of tetraneopentylchromium under carbon monoxide,[9] but the identity and reactivity of the primary photoproduct have not been established. The high symmetry of the tetraalkyl complexes should lead to a simpler absorption spectrum, and because only alkyl ligands are present, potential interfering absorptions and photoprocesses due to other ligands should be prevented from obscuring those due to metal–alkyl bonding. The results presented here support these conclusions.

The widest series of tetraalkyl complexes of a single ligand that has been prepared are the tetranorbornyl complexes of the elements titanium through cobalt. Photolysis of these complexes has been reported to yield binorbornyl and norbornane;[10] this, coupled with their exceptional thermal stability,[1,10] led to their selection for a detailed study of the photochemistry of homoleptic metal alkyls. In this paper are reported the spectroscopy and photochemistry of the two most accessible members of this series. Preliminary accounts of this work have appeared.[11]

Results

The tetranorbornyl complexes of titanium (I) and chromium (II) are the most stable of the series titanium through cobalt first synthesized by Bower and Tennent.[10,12] Although the chromium complex behaves as they described, tetranorbornyltitanium seems to be slightly less stable, decomposing slowly in air at room temperature to



$\equiv M(NOR)_4$

I, M = Ti
II, M = Cr

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† Summer Undergraduate Research Program participants.

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(2) Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979; Chapter 8.

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(7) Ballard, D. G. H.; van Lienden, P. W. *Makromol. Chem.* **1972**, *154*, 177–190.

(8) Chien, J. C. W.; Wu, J.-C.; Rausch, M. D. *J. Am. Chem. Soc.* **1981**, *103*, 1180–1185.

(9) Mintz, E. A.; Rausch, M. D. *J. Organomet. Chem.* **1979**, *171*, 345–351.

(10) Bower, B. K.; Tennent, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512–2514.

(11) (a) Abrahamson, H. B.; Dennis, E. *J. Organomet. Chem.* **1980**, *201*, C19–C23. (b) Abrahamson, H. B.; Martin, M. E. *Ibid.* **1982**, *238*, C58–C62.

(12) Bower, B. K. U.S. Patent 3705916, 1972.

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Table I. Electronic Spectral Features of $M(NOR)_4$ [a]

M	band max, nm (ϵ, M^{-1} cm^{-1})	assignment [b]
Ti	245 (29 200)	$^1A_1 \rightarrow {}^1T_2$ ct
	286 (sh)	$^1A_1 \rightarrow {}^1T_1$ ct
	367 (253)	$^1A_1 \rightarrow {}^1E$ ct
	412 (sh)	ct
Cr	265 (29 700)	$^3A_2 \rightarrow {}^3T_1$ ct
	294 (sh)	$^3A_2 \rightarrow {}^3T_1$ ct
	335 (sh)	$^3A_2 \rightarrow {}^3T_2$ ct
	486 (1340)	$^3A_2 \rightarrow {}^3T_1$ lf
	534 (sh)	$^3A_2 \rightarrow {}^1E$ sp
	553 (sh)	$^3A_2 \rightarrow {}^1E$ sp
	620 (sh, 270)	$^3A_2 \rightarrow {}^3T_2$ lf

[a] Hexane solution, 25 °C. [b] State designations based on full tetrahedral symmetry: ct = ligand-to-metal charge-transfer, lf = ligand field, and sp = ligand field spin pairing. See text for a discussion of the assignments.

an unidentified white solid.[13] Consequently, the titanium complex is normally stored at −25 °C under a nitrogen atmosphere, which alleviates the problem. Measurement of the magnetic susceptibility of the complexes by the Evans method[14] in toluene solution indicates magnetic moments of 0.00 and 2.86 μ_B for I and II, respectively. Both complexes are soluble in common organic solvents, including hexane, carbon tetrachloride, toluene, tetrahydrofuran, and dichloromethane, but are insoluble in more polar solvents such as methanol, water, and acetonitrile.

Spectroscopy. The titanium complex I is light yellow, the only absorption in the visible region of the spectrum being a weak tail of the intense bands in the ultraviolet. The chromium complex II, on the other hand, is deep purple, a consequence of a relatively intense band system in the visible region of the spectrum. Quantitative electronic spectral data for both complexes are presented in Table I. The ultraviolet absorptions of both complexes exhibit a blue shift with cooling to liquid-nitrogen temperatures (see Figure 1). In the visible band system of the chromium complex, only some of the weaker components shift with changes in temperature.

Solvent shifts for most features in the absorption spectrum are minimal. Band positions and intensities for both the visible and ultraviolet systems in II are nearly identical in tetrahydrofuran when compared to the values for hexane. The only significant deviation is in the position of the lowest energy shoulder that shifts to 617 nm in THF. Dilution of a hexane solution of II with either carbon tetrachloride or ethanol results in a small shift (+0.5 nm) in the 486-nm band maximum; the shifts in the 265-nm band are in oppposite directions (ethanol, −0.6 nm; CCl_4, +0.8 nm) but are still small. Shifts in the $Ti(NOR)_4$ spectrum are similar to those of the ultraviolet band in II. For the 367-nm band in I, ethanol gives a −3.8-nm shift and CCl_4 a +1.2-nm shift. For the 245-nm band, ethanol gives a −0.2-nm shift, while CCl_4 absorbs too much to observe the shift.

Photochemistry. Irradiation of hexane solutions of either complex in the presence of air leads to extensive and immediate decomposition accompanied by the deposition of a flocculent precipitate (white for I, gray for II). If air is rigorously excluded by freeze–pump–thaw cycles, solutions remain clear during the initial portions of photolysis but a small amount of solid material is produced with longer photolysis times (green for I, tan for II). If carbon tetrachloride is included in the solution at levels between 0.1 and 1.0 M, the formation of these solid products can be reduced in the titanium case and totally eliminated in the chromium case. In CCl_4 solution, spectral changes in the visible region are clean. Complex I has an isosbestic point at 430 nm, with increasing absorbance at 600 nm and decreasing absorbance in the 350–430-nm region as a result of photolysis. In II, there is an isosbestic point at 479 nm, increasing absorbance in the 400–479-nm range and decreasing at longer wavelengths, resulting in a color change from purple to orange. In hexane and tetrahydrofuran, irradiation results in weak increases in the near-infrared, with maxima at 950 and 820 nm, respectively, and isosbestic points at about 700 nm; extinction coefficients for these bands are less than 250 L (mol of Cr)$^{-1}$ cm^{-1}.[15]

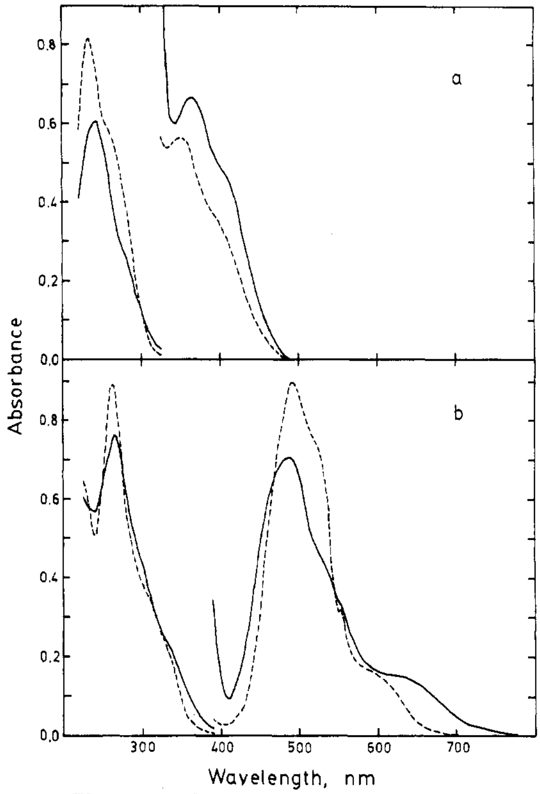

Figure 1. Electronic absorption spectra of $M(NOR)_4$ (a, M = Ti; b, Cr) in EPA solvent (5:5:2 diethyl ether/isopentane/ethanol). Solid lines are the room-temperature spectra, and the dashed lines are the spectra at 77 K. The low-temperature spectrum has been corrected for solvent contraction. The portion to the right used a more concentrated sample (130 times for a and 22 times for b).

Quantum Yields. Quantum yields for disappearance of the tetranorbornyl complexes under various conditions are listed in Table II. Note the similarity of the quantum yields for both complexes in the ultraviolet region and the decrease in quantum yield in the chromium complex as longer wavelength visible light is used. The disappearance of $Cr(NOR)_4$ can be monitored by following the decline of the shoulder at 620 nm, as this region is free of product absorption in hexane solution. However, optical quantitation of $Ti(NOR)_4$ is impossible due to the absorption of uncharacterized products in the same region as the starting material. Consequently, a liquid chromatographic method has been developed to separate unreacted starting material

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(13) In all cases, samples of tetranorbornyltitanium gave good elemental analyses, were diamagnetic, and gave mass spectra consistent with the $Ti(NOR)_4$ formulation. See Experimental Section.

(14) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005. (b) Deutsch, J. L.; Poling, S. M. *J. Chem. Educ.* **1969**, *46*, 168–169. (c) Loliger, J.; Scheffold, R. *Ibid.* **1972**, *49*, 646–647.

(15) The near-infrared band grows in at a rate slower than that at which the shoulder at 620 nm is disappearing.

Table II. Quantum Yields for Disappearance of $M(NOR)_4$[a]

M	λ, nm	$[M(NOR)_4]$,[b] mM	$[CCl_4]$,[c] M	ϕ[d]	method[e]
Cr	254	1.4		0.040 (11)	o
		2.3		0.038 (4)	o
	313	0.6		0.037 (2)	c
		1.4		0.045 (14)	o
		1.3	10.3	0.033 (2)	o
		6.6	10.2	0.031 (4)	o
	366	0.6		0.035 (9)	c
		1.0		0.044 (7)	c
		1.0		0.032 (4)	o
		1.4		0.044 (12)	c
		2.4		0.035 (9)	c
		0.7	1.0	0.035 (2)	o
		1.4	1.0	0.033 (5)	o
		2.6	1.0	0.036 (2)	o
		5.6	10.3	0.042 (2)	o
	436	0.7		0.0038 (9)	o
		3.5		0.0040 (5)	o
		0.6	10.3	0.0032 (9)	o
	488	6.6	0.1	0.0007 (2)[f]	o
	550	3.6		0.00023 (8)	o
		3.4	1.0	0.00026 (7)	o
	633	0.6		<0.000004[f,g]	o
Ti[h]	254	2.9		0.042 (8)	c
	313	0.8		0.065 (18)	c
		1.3		0.047 (20)	c
	366	0.5		0.052 (3)	c
		3.6		0.047 (21)	c
		4.6		0.038 (21)	c
		5.7		0.037 (10)	o[i]
		6.9		0.017 (7)	o[i]

[a] In hexane solution, except as noted. Quantum yields calculated by the differential method described in the Experimental Section and are corrected for incomplete absorption and the inner filter effect.
[b] Determined by absorption measurements on unirradiated solution. [c] Neat CCl_4 is 10.3 M, 10.2 M indicates the presence of 0.1 M decane used in gas chromatography experiments. [d] Standard deviation of last digit in parentheses. [e] o = concentration determined by optical measurements; c = concentration determined by liquid chromatography. [f] Approximate yield. Light intensity derived from power of laser. [g] Quantum yield is a lower limit. No change detected after 1 week of HeNe laser irradiation. [h] Quantum yields for $Ti(NOR)_4$ not corrected for inner filter effect.
[i] Optically determined quantum yields are a lower limit only, due to uncorrected product absorption at the analysis wavelength.

and quantitate it.[16] This method has also been used for some determinations of $Cr(NOR)_4$ disappearance quantum yields (see Table II) and gives values identical with those obtained by absorbance measurements.

Organic Products. Analysis of the products of the photolysis of both I and II using gas chromatography and GC/MS techniques indicates that the organic products in hexane are norbornane and 1,1′-binorbornyl as reported by Bower and Tennent.[10] However, when the organic products are separated from the metal-containing products by trap-to-trap distillation on a high vacuum line and the distilled fraction subjected to gas chromatographic analysis, only norbornane is observed. (Authentic mixtures of organic products transfer with greater than 90% recovery.) The binorbornyl observed in normal injections must come from thermal decomposition of nonvolatile products in the injection port of the gas chromatograph; injection of unirradiated hexane solutions of II does not produce binorbornyl. The quantum yield for production of norbornane by photolysis of II in hexane is 0.071 ± 0.015 (see Experimental Section).

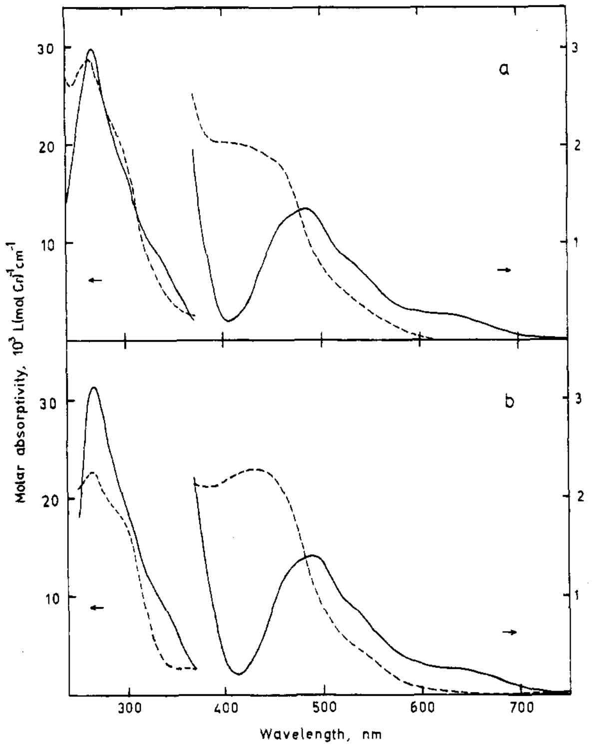

Figure 2. (a) Difference absorption spectrum of a solution of $Cr(NOR)_4$ initially 6.3×10^{-3} M in hexane and irradiated for 131 min with the 366-nm source. Reference is a 5.4×10^{-3} M solution of $Cr(NOR)_4$ in hexane. (Calculated concentration of product is 0.88×10^{-3} M.) Cell path length is 0.100 cm on the right and 0.0100 cm on the left. (b) Similar difference spectrum in CCl_4 solution. Initial concentration was 5.82×10^{-3} M, and reference is 4.35×10^{-3} M; calculated product concentration is 1.53×10^{-3} M. Dashed lines are difference spectrum, and solid lines are spectra of II for comparison.

Table III. Electronic Spectral Parameters for $Cr(NOR)_4$ Photoproducts

solvent	band max, nm (ϵ, M^{-1} cm^{-1})[a]	solvent	band max, nm (ϵ, M^{-1} cm^{-1})[a]
hexane	262 (29 000)	CCl_4	263 (22 600)
	290 (sh)		295 (sh)
	420 (sh, 2000)		429 (2300)

[a] Extinction coefficients per chromium, derived from difference spectra (Figure 2); quantitative chemical yield of photoproduct is assumed.

Analysis of the organic products of the photolysis of I and II in carbon tetrachloride indicates the production of norbornane, 1-chloronorbornane, hexachloroethane, 1,1′-binorbornyl, and traces of 1-(trichloromethyl)norbornane. A trap-to-trap distillation to separate the organic products from metal-containing products transfers only the last four compounds, indicating that the norbornane must come from the thermal decomposition of nonvolatile species in the injection port of the gas chromatograph. Unirradiated CCl_4 solutions of II, in contrast to hexane solutions, do decompose in the GC injection port, producing some binorbornyl. Correcting for the decomposition of metal-containing reactants and products, the quantum yields for the appearance of the organic products in CCl_4 are 0.008 ± 0.001 (1-chloronorbornane), 0.026 ± 0.002 (hexachloroethane), and 0.014 ± 0.001 (1,1′-binorbornyl).

Metal-Containing Photoproduct Characterization. Attempts to isolate the orange photoproduct of II are unsuccessful (see Experimental) but when generated in

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(16) Abrahamson, H. B.; Vanderpool, R. A. *Anal. Chim. Acta* 1984, *159*, 355–358.

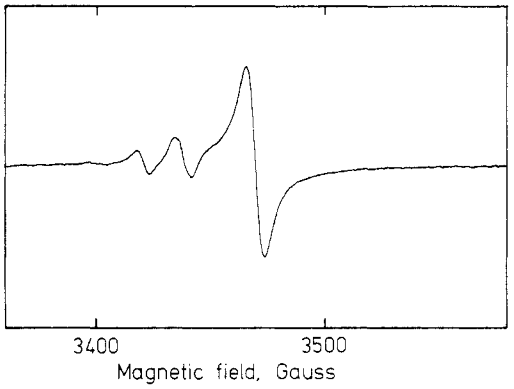

Figure 3. Electron spin resonance spectrum of Ti(NOR)$_4$ in toluene solution, freeze–thaw degassed and flame sealed in a 4-mm quartz tube and irradiated for 5 min with the broad-band ultraviolet source. Spectrum was taken at ambient temperature with klystron frequency equal to 9.480 GHz. For the most intense line, $g = 1.95$. The same solution showed no detectable resonances before irradiation.

CCl$_4$, the photoproduct does appear to contain chlorine. Difference electronic spectra (Figure 2) can be obtained from partially photolyzed solutions of II, and extinction coefficients can be calculated (Table III). Similar photoproduct absorptions are seen in both hexane and CCl$_4$. The magnetic susceptibility of II shows no change as a function of irradiation time, indicating an average of two unpaired electrons per chromium in the photoproduct. Attempts to observe the electron spin resonance spectrum of the photoproduct of II are unsuccessful, as photolysis merely reduces the intensity of the resonance[17] due to II.

In contrast, irradiation of flame-sealed quartz tubes of I in toluene solution produces a complex spectrum (Figure 3). This signal decays after standing in the dark with the high-field portion fading more quickly than the less intense features at lower field. Stable solutions of the titanium-containing photoproducts could not be generated, making it difficult to obtain optical difference spectra in the manner done for chromium.

Discussion

The analytical data and magnetic susceptibility results are consistent with the formulation of these complexes as M(NOR)$_4$ (I, M = Ti; II, Cr). Their solubility behavior and simple spectra indicate that they have a high symmetry. Attempts to build models of these compounds indicate that only configurations approximating tetrahedral symmetry will be stable due to steric crowding. Both complexes form nice crystals, but attempts to solve the crystal structures have so far been unsuccessful. The data to date are consistent with near T_d symmetry around the metal but seem to be complicated by severe disorder problems.[18] Electron spin resonance studies of related MR$_4$ complexes indicate that D_{2d} symmetry is more likely.[19]

Assignment of Ultraviolet Band System. As expected, the spectra are relatively simple, and the absence of interferences allows some reasonable assignments to be made. The shift of the ultraviolet bands to higher energies in more polar solvents is consistent with an excited state that is less polar than the ground state. These solvent shifts, their blue shift when solutions are cooled to 77 K, and the lack of visible absorptions in the titanium complex allow the assignment of the ultraviolet absorptions in both of the complexes as due primarily to ligand-to-metal charge-transfer (LMCT) transitions (see Figure 4). In strict tetrahedral symmetry, the only LMCT transition that is orbitally allowed in the d^0 complex I is $^1A_1(a_1^2t_2^6) \rightarrow {}^1T_2(a_1^2t_2^5e^1)$,[21] and the observed extinction coefficients require that the most intense absorption (245 nm) receive this assignment. The $^1A_1 \rightarrow {}^1T_1(a_1^2t_2^5e^1)$ transition is orbitally forbidden in a tetrahedral complex, as is $^1A_1 \rightarrow {}^1E(a_1^1t_2^6e^1)$. Reduction of symmetry to, e.g., D_{2d},[19] results in the splitting of $^1T_1$ into ^1E and $^1A_2$. Under the lower symmetry, the $^1A_1 \rightarrow {}^1E$ component is orbitally allowed and is thus expected to be more intense than under strict tetrahedral symmetry. This is a potential explanation for the shoulders on the intense ultraviolet band in Ti(NOR)$_4$. The $^1T_2$ state will also be split under D_{2d} symmetry, into ^1E and $^1B_2$, transitions to both of which will still be allowed from the A_1 ground state. Note that an additional component may be present on the high-energy side of the 245-nm band. The lowest energy band at 367 nm is likely due to the $^1A_1 \rightarrow {}^1E$ transition, which remains forbidden even under D_{2d} symmetry. This assignment requires the filled a_1 level to lie higher than the filled t_2, to give a lower energy absorption than the $^1A_1 \rightarrow {}^1T$ components do. This seems reasonable from simple overlap arguments.[20] Alternative assignments for the weak bands could include spin-forbidden counterparts of the allowed transitions discussed above.

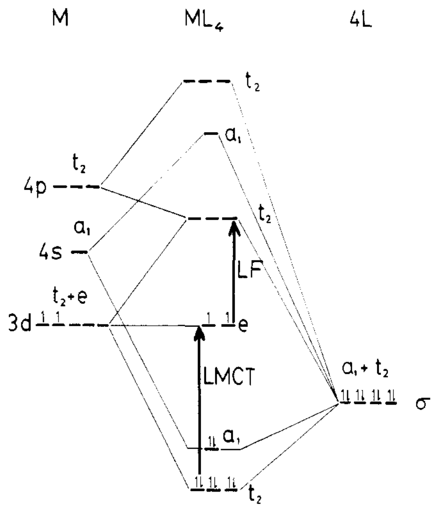

Figure 4. Qualitative molecular orbital diagram for a tetrahedral complex considering only σ bonding. Electron occupancy shown is for M = Cr; for M = Ti the two electrons in the e symmetry orbital are absent.

The corresponding assignments in the chromium complex II are $^3A_2(a_1^2t_2^6e^2) \rightarrow {}^3T_1(a_1^2t_2^5e^3)$ fully allowed, with $^3A_2 \rightarrow {}^3T_2(a_1^2t_2^5e^3)$ and $^3A_2 \rightarrow {}^3E(a_1^1t_2^6e^3)$ orbitally forbidden. Reduction of symmetry to D_{2d} again splits the degenerate states, and $^3B_1 \rightarrow {}^3E$ (derived from $^3A_2 \rightarrow {}^3T_2$ in T_d) becomes allowed, resulting in a situation paralleling that of the titanium complex. Qualitative explanations, such as the expected size differential between Ti(IV) and Cr(IV)[22a] (which has been confirmed by preliminary

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[17] Ward, G. A.; Bower, B. K.; Findlay, M.; Chien, J. C. W. *Inorg. Chem.* **1974**, *13*, 614–617.

[18] Results confirming these have been obtained independently for the chromium complex II: Rheingold, A., private communication, Sept 1983.

[19] Mowat, W.; Shortland, A. J.; Hill, N. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 770–778.

[20] Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977; p 542.

[21] Figgis, B. N. "Introduction to Ligand Fields"; Wiley-Interscience: New York, 1966.

crystallographic results), lead one to predict a higher energy allowed LMCT transition in II vs. I. That there is instead a 3100-cm^{-1} decrease in the position of the most intense transition in going from I to II indicates that a more complex relation exists between the ground- and excited-state potential surfaces in these complexes.[22b]

Assignment of Visible Band System in $Cr(NOR)_4$. It is difficult to unambiguously assign most of the rest of the features of the absorption spectra of II. However, on the basis of the insensitivity to temperature and solvent changes of the 486-nm band and its absence in I, the assignment of this absorption to a ligand field transition is the most reasonable. Two triplet excited states are derived from the $e^1t_2^1$ configuration, $^3T_2$ and $^3T_1$ ($^3T_1$ higher in energy[21]). In other chromium tetraalkyls, which have similar visible spectra, the most intense components of the visible band have been assigned to $^3B_1 \rightarrow {}^3E(T_1)$ and $^3B_1 \rightarrow {}^3A_2(T_1)$ transitions[19] under the assumed D_{2d} symmetry, both of which should be allowed. In those $Cr(R)_4$ complexes (R = methyl, neopentyl, (trimethylsilyl)methyl, and tritylmethyl) there is a separation of 2200–2700 cm^{-1} between two reconstructed components, with the stronger at shorter wavelengths. In contrast, the separation between the components of the visible band in II is only 1200 cm^{-1}. This brings earlier observations into question, especially since $Cr(neopentyl)_4$ is found to have an electronic spectrum very similar to that of $Cr(NOR)_4$,[25] instead of that found earlier.[19]

We find instead that reconstruction of the visible spectrum of $Cr(NOR)_4$ with a sum of Gaussians[23] requires a minimum of five components, corresponding roughly to the four bands obvious in the low-temperature spectrum (Figure 1) plus one at approximately 460 nm. A low-temperature spectrum of $Cr(neopentyl)_4$[25] reveals that it too, in reality, has a similarly complex band structure but that $Cr(NOR)_4$ (Figure 1b) retains considerably more of that structure in its room temperature electronic spectrum than does the neopentyl complex. The fact that some of the weaker features are visible in the norbornyl complex even at room temperature implies that there may be some distortion of this molecule at room temperature that is not present in the less hindered neopentyl congener. The lowest energy transition is likely due to $^3A_2 \rightarrow {}^3T_2$ which would become allowed upon reduction of symmetry to D_{2d} ($^3B_1 \rightarrow {}^3E$). Spin-pairing transitions such as $^3B_1 \rightarrow {}^1A_1$ and $^3B_1 \rightarrow {}^1B_1$ derived from $^3A_2 \rightarrow {}^1E$ in T_d may give rise to the weak features between 500 and 600 nm; other spin-forbidden transitions are likely too high in energy.[21]

Photochemistry. In most of the studies of metal alkyl photochemistry to date,[2] homolytic cleavage of the metal alkyl bond has been proposed as the primary photoprocess on the basis of typical alkyl radical products. The analyses of organic products of the photochemistry reported here are consistent with a similar assignment for the primary photoprocess in these complexes

$$M(NOR)_4 \xrightarrow{h\nu} NOR\cdot + \text{“}M(NOR)_3\text{”} \qquad (1)$$

because typical radical coupling (1,1′-binorbornyl) and abstraction (norbornane, chloronorbornane) products are observed. Disproportionation products are not seen and are not expected because of Bredts' rule.[26]

The quantum yields for disappearance of I and II are very similar for ultraviolet irradiation (Table II). (Differences between these values and those reported earlier[11] can be accounted for by a more accurate correction for the inner filter effect (see Experimental Section).) This lends credence to the similar assignment to the ultraviolet band systems as due to LMCT transitions in both of these complexes. The very low quantum yields observed for visible light photolysis indicates that the ligand field excited states in II do not appreciably labilize the chromium–norbornyl bond. The primary photoprocess outlined in eq 1 is the logical consequence of a LMCT excitation, resulting in a formal reduction of the metal and formal oxidation of the two-electron donor NOR^- ligand. The lack of a dependence of the quantum yields for disappearance of II on the concentration of the radical trapping agent carbon tetrachloride further reinforces the dissociative nature of the primary photoprocess and its conservation between the two solvents. Apparently every cage escape leads to decomposition, but the product distribution is different in the two solvents.

The relatively low values of the quantum yields, even with ultraviolet irradiation, indicate that other deactivation pathways are more accessible to the LMCT excited state(s). These other pathways must be assigned to nonradiative decay, since no emission can be observed from solutions of II at room temperature. In II one can postulate the decay of the LMCT excited state to the lower energy nonphotoactive LF states as another possible decay path leading to low quantum yields. However, this route is not available to I, and the quantum yields for its dissociation are only slightly higher than those for II. If one assumes that the UV quantum yield for product formation from II in the absence of LMCT to LF crossing is the same as the UV quantum yield for I, then yields of intersystem crossing (0.26) and nonradiative decay (0.70) from the LMCT state can be calculated for II.

In eq 1 the metal-containing product is written as "$M(NOR)_3$" because the complex produced by the photolysis of II is obviously not $Cr(NOR)_3$, which should be green and have three unpaired electrons, based on other known trialkylchromium complexes.[1,10] In contrast, the material produced from $Cr(NOR)_4$ photolyses is orange with two unpaired electrons per chromium. The differences in stability, spectra, and residual norbornyl content indicate that the identity of the photoproducts made in the different solvents are not the same, though neither is $Cr(NOR)_3$.

Interpretations of the types and amounts of organic photoproducts of irradiation of the title compounds are complicated by the thermal instability of the metal-containing photoproducts, whose decomposition in the injection port of the gas chromatograph gives additional organic compounds of the same type as generated by the photoreactions. Separation of the organic photoproducts on the high-vacuum line allows the identification of those that are produced solely by irradiation. The production of norbornane in neat CCl_4 and of binorbornyl in hexane can by this means be attributed to the decomposition of norbornyl-containing metal complex photoproducts in the 250 °C injection port of the GC.

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(22) (a) Less complete shielding of the nuclear charge by the electrons in the d orbitals leads to a reduced radius of the M(IV) ion for chromium compared to titanium (see, e.g., ref 20, pp 528 and 555). This should result in a reduced metal–ligand distance and should increase metal–ligand orbital overlap and cause a larger gap between filled ligand orbitals and the metal d orbitals. (b) We thank a reviewer for noting that changes in the electron repulsion component of the LMCT energy may contribute to the difference between I and II.

(23) Summations were performed by using portions of a deconvolution program[24] adapted for use on the IBM 3081.

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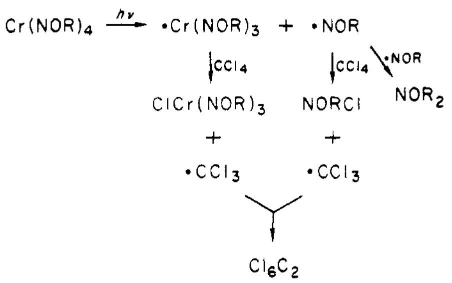
Scheme I



The quantum yield for the photoproduction of norbornane from hexane solutions of II is 0.071, which is nearly twice that seen for the disappearance of the tetraalkyl (0.04). This indicates that two norbornyl radicals are formed in the photolysis of each $Cr(NOR)_4$. The initial photoreaction is most likely a loss of one norbornyl radical, forming $Cr(NOR)_3$ as a transient species. This intermediate either could abstract a hydrogen from solvent and suffer a subsequent reductive elimination of norbornane or may thermally lose a second norbornyl radical. In either case the result is the overall loss of two norbornyl ligands per chromium. The ultimate metal-containing photoproduct will likely suffer oligomerization or reactions with solvent in an attempt to fill the coordinative unsaturation.

In carbon tetrachloride, the net quantum yield for the production of norbornyl radicals (that for chlornorbornane plus twice the yield for binorbornyl, 0.036) is the same as the quantum yield for the disappearance of chromium complex II. This indicates that, in contrast to the course of events in hexane, only one norbornyl ligand is lost per chromium in CCl_4 solution. This may reflect a difference in the stability of the products of the subsequent thermal reactions of the putative $Cr(NOR)_3$ in the two solvents. Note that the abstraction of chlorine from CCl_4 by the norbornyl radical does not appear to be very efficient, as the coupling of the norbornyl radicals is more prevalent than abstraction, giving a higher yield of binorbornyl than of chloronorbornane.

In addition, the quantum yield for the production of trichlorocarbon radicals (0.052) is equal to the sum of the yield of chloronorbornane (0.008) and that for the production of $Cr(NOR)_3$ (assumed equal to disappearance of $Cr(NOR)_4$, 0.04). This is consistent with the attack of solvent CCl_4 by the $Cr(NOR)_3$ intermediate to form $ClCr(NOR)_3$ (Scheme I). It is conceivable that the thermal decomposition of this or a related species will give different organic products from those generated by the decomposition of the product from irradiation in hexane, as has been observed. The observation of chloride upon digestion of the nonvolatile products is further evidence for bound chlorine in the metal photoproduct, presumably $ClCr(NOR)_3$.

Magnetic susceptibility results are consistent with a Cr(IV) product or with a dimeric Cr(III) product, but the lack of separation upon size exclusion chromatography of photolyzed solutions of II argues against the latter formulation. While the form of the photoproduct is likely $ClCr(NOR)_3$ in CCl_4 solutions, the form in alkane or arene solvents is less certain and appears to be less stable. The lack of an ESR signal due to the chromium product is not a major difficulty, since low temperatures may be necessary to observe it. The observation of a signal in irradiated toluene solutions of I indicates that there is produced a paramagnetic product, likely metal centered from the g value,[8] that has some stability. This may be $Ti(NOR)_3$, but confirmation of this supposition will be difficult. The long wavelength absorptions of the photoproducts can be attributed to some transition where the excited state is destabilized in polar media, which implies substantial solvent interaction.

Conclusions. The photoinduced loss of norbornyl ligands in the title complexes can be attributed to the homolytic cleavage of a metal ligand bond resulting from a ligand-to-metal charge-transfer excited state. The absorptions corresponding to these excited states are found in the ultraviolet regions of the spectrum, and the visible region ligand field transitions in $Cr(NOR)_4$ are substantially photoinactive. The balance of organic products implies that the the product from the photolysis of $Cr(NOR)_4$ in CCl_4 is of the form $ClCr(NOR)_3$; independent confirmation of this hypothesis is difficult. Exact formulations for photolysis products from $Cr(NOR)_4$ in other solvents and from $Ti(NOR)_4$ are more speculative.

Experimental Section

Materials and Equipment. Reagent grade hexane was purified as previously described.[16] Following literature procedures, norbornyl chloride was prepared from norcamphor[27] and $CrCl_3(THF)_3$[28] and $TiCl_4(THF)_2$[29] were prepared from the respective anhydrous chlorides. Other commercially available chemicals were at least reagent grade and were used as received. Electronic absorption spectra were recorded on Cary 118 and Hitachi-Perkin Elmer 100-80 spectrophotometers. Near-infrared spectra were recorded on a Cary 14 spectrophotometer. Spectra at liquid-nitrogen temperature were recorded in quartz cells in a locally constructed all-quartz Dewar with optical flats as windows. Mass spectra were collected with a Hewlett-Packard 5895 GC/MS/DS. Electron spin resonance were recorded at the University of Arkansas on a Varian E-4 instrument (X-band) in cylindrical 4-mm diameter quartz tubes degassed by freeze–pump–thaw cycles (10^{-5} torr) and flame sealed. NMR spectra were collected on a Varian T-60 instrument.

Irradiation sources are medium-pressure mercury arc lamps (Hanovia) in water-cooled quartz jackets. The appropriate spectral lines are isolated with Corning filters with a 3.4 mM K_2CrO_4 solution (path = 1.1 cm) added for 313-nm irradiations. The source for the 633-nm irradiation is a Spectra-Physics 145-01 4-mW HeNe laser, and the 488-nm source is a 5-W argon ion laser. Irradiations at 254 nm are performed with an unfiltered low-pressure mercury lamp with spectral purity >85%.[30] Broad-band irradiations use a Ultra-Violet Products XX-15 fixture with two GE long-wave ultraviolet lamps (maximum output ~350 nm).

Synthesis of 1-Norbornyllithium. The method used is a modification of that described in ref 12. A 250-mL two-necked flask was equipped with a mechanical stirrer, half filled with 3-mm diameter glass beads, and fitted with a reflux condenser topped by a Claisen adapter with a septum and gas inlet. The apparatus was degassed on the Schlenk line, and an excess of lithium metal wire (0.5 g, 72 mmol) cut into small pieces under nitrogen was added. Degassed hexane was added to just cover the beads (about 100 mL), and the mixture was brought to reflux and stirred vigorously for 1 h. At that time 4.63 g (35 mmol) of 1-chloronorbornane (in hexane, freeze–thaw degassed) was added via cannula, and the mixture was refluxed with continued vigorous stirring for an additional 3 h. After being cooled, the solution was transferred to the drybox, decanted from the beads, and centrifuged. The supernatant from the centrifugation step was decanted into a Schlenk flask and the solvent removed by pumping. The flammable white solid (1.41 g, 13.8 mmol, 39% yield) is stored at room temperature under nitrogen.

Synthesis of Tetranorbornylchromium. The method of Chien et al.[17] was used for some preparations, but higher yields were obtained from the following procedure. In the drybox, 0.20

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(30) Intensities above and below 300 nm compared by doing actinometry in quartz (I_Q) and Pyrex (I_P) cells; $I_P/I_Q < 0.15$.

g (16.5 mmol) of 1-norbornyllithium was dissolved in 150 mL of hexane. With continuous stirring, 0.47 g (1.25 mmol) of $CrCl_3(THF)_3$ was added all at once. The mixture was stirred until all of the chromium complex had dissolved, about 48 h. The solution was then centrifuged to remove LiCl, and the supernatant was applied to a column of grade I alumina (Sigma) and eluted with hexane. The purple fractions were combined, evaporated, and sublimed at 100 °C and 5×10^{-6} torr to yield 0.245 g (0.57 mmol) of pure $Cr(NOR)_4$, a 46% yield. Elemental analysis (Schwarzkopf) of a purified sample was excellent. Calcd for $C_{28}H_{44}Cr$ (found): C, 77.73 (77.65); H, 10.25 (10.13). The mass spectrum has a parent ion at *m/e* 428 and multiplets at *m/e* 333, 238, and 143 with a chromium isotope pattern, corresponding to successive loss of norbornyl groups. No NMR spectrum could be recorded due to the paramagnetism of the complex.

Synthesis of Tetranorbornyltitanium. The synthetic method for $Cr(NOR)_4$ (above) was used. A typical preparation using 2.84 g (27.8 mmol) of LiNOR and 2.09 g (6.3 mmol) of $TiCl_4(THF)_2$ yielded 0.97 g (2.3 mmol) of yellow $Ti(NOR)_4$, a 33% yield. The complex was purified by chromatography on silical gel or neutral alumina and recrystallized from hexane. Elemental analysis (Galbraith) of a purified sample was excellent. Calcd for $C_{28}H_{44}Ti$ (found): C, 78.47 (78.33); H, 10.35 (10.30); Ti, 11.18 (11.19). Mass spectrum has a weak parent ion at *m/e* 428 and multiplets at *m/e* 333, 238, and 143 with a titanium isotope pattern, corresponding to successive loss of norbornyl groups.

Synthesis of 1,1′-Binorbornyl. A new method based on a cuprate reagent[31] was developed to replace previous low yield syntheses.[32] Under a dry nitrogen atmosphere, 0.690 g (6.76 mmol) of norbornyllithium and 0.645 g (3.39 mmol) of cuprous iodide (Fisher) were stirred in 50 mL of hexane for 4 h. At that time, 0.440 g (3.37 mmol) of 1-chloronorbornane was added dropwise. Gas chromatography was used to follow the course of the reaction. As production of the coupled product slowed, additional cuprous iodide was added in 2-g portions. A total of 9.6 g was added (15-fold excess) over a 6-day period with occasional stirring. At the end of the 6 days, the mixture was centrifuged and the clear supernatant was removed from the drybox. This hexane solution was then washed with distilled water, dried over magnesium sulfate, and filtered and the solvent removed by slow evaporation at room temperature. The resultant clear crystals were sublimed under vacuum onto a −78 °C cold finger to yield 0.28 g (1.5 mmol, 44%) of pure 1,1′-binorbornyl. Purity of the product was confirmed by gas chromatography and mass spectroscopy.

Photochemical Procedures. The solutions used for quantum yield determinations were either deaerated by purging with a stream of nitrogen or degassed by at least three freeze–pump–thaw cycles on a high vacuum line. Samples were irradiated in a 1-cm quartz cuvette when followed spectroscopically (3.0-mL sample) or in Pyrex or quartz ampules (4.0-mL sample) for chromatographic quantitation. The irradiated solutions were thermostated at 25 °C. The progress of the photoreaction was followed either optically at 620 nm and at the irradiation wavelength or by the liquid chromatographic method developed in this laboratory,[16] and concentrations were calculated at different irradiation times. Lamp intensities were measured by ferrioxalate (all wavelengths)[33] and Reinekate (546-nm)[34] actinometry.

Photochemical Calculations. Quantum yields were calculated in a differential manner, using changes in reactant concentration to calculate a disappearance yield for each irradiation time. Corrections were made for the incomplete absorption of the starting material and the inner filter effect where appropriate[35] (possible only for II). Ten points with intervals of about 1% conversion were normally taken; a total conversion of less than 15% was used to avoid secondary photolysis. The quantum yield for each interval was calculated by using the equation[35]

$$\Phi = \frac{([R]_i - [R]_{i-1})V(\epsilon_R[\bar{R}] - \epsilon_p[\bar{P}])}{(t_i - t_{i-1})I_0\,(1 - 10^{-\bar{A}})(\epsilon_R[\bar{R}])} \qquad (2)$$

The terms $[\bar{R}]$ and $[\bar{P}]$ are the average concentrations of the reactant and product, respectively, and $\bar{A}$ is the average absorbance at the irradiated wavelength for the time interval t_{i-1} to t_i. The extinction coefficients (ϵ) are for the reactant (ϵ_R) and the product (ϵ_p) at the irradiation wavelength, and V is the volume of irradiated solution. I_0 is the incident light intensity. Multiple determinations were done under similar conditions for most cases, and the weighted average was calculated. The standard deviations shown in Table II are those for the weighted mean.

Organic Product Quantitation by Gas Chromatography. Pure samples of the expected photoproducts (norbornane, binorbornyl, norbornyl chloride, and hexachloroethane) were used for calibration. Decane or dodecane (Aldrich Gold Label) was used in a known amount (less than 0.1% by volume) as an internal standard. Ratios of peak areas (height times fwhm) to internal standard peak areas were plotted vs. the corresponding concentration ratios; these calibration plots were linear.

Solutions of metal alkyls were freeze–thaw degassed and then backfilled with nitrogen in a special cell that allows small microliter aliquots to be extracted through a septum-sealed side arm. Before irradiation began and after each irradiation period (366 nm, typically 20 min) an liquot (10 μL) was withdrawn and injected onto a SE-30 column (3.8% on Chromosorb W, $^1/_8$ in. × 6 ft stainless steel). Use of a temperature program (10 °C/min, 30–200 °C) allowed the elution of all peaks within 20 min. Concentrations were calculated by using the calibration plots described above.

Attempted Isolation and Characterization of Metal-Containing Photoproducts. Attempts to isolate the orange chromium photoproducts have been unsuccessful. Extraction with solvents like acetonitrile and acetone, in which the unreacted II is insoluble, followed by evaporation of the extracting solvent invariably leads to intractable oils or solids of low stability. Materials photogenerated in CCl_4 solvent are marginally more stable than those generated in hexane. Chromatography on alumina or silica gel allows separation of unreacted starting material, which elutes close to the solvent front,[16] but the orange photoproduct is retained at the top of the column. An orange band can sometimes be eluted with methanol but again produces only oils upon evaporation. Size exclusion chromatography (toluene solvent, Bio-Beads S-X12 styrene–divinylbenzene 12% cross-linked resin) was also attempted on the theory that the photoproduct contains two or more metal atoms but produced no detectable separation. All of these attempted isolation procedures were complicated by the extreme air sensitivity of the photoproducts.

The magnetic susceptibility of the photoproduct was estimated by measuring the shift of the proton resonance of benzene (1% in CCl_4) caused by the paramagnetism of II (Evans method[14]). Irradiation for 1 h of 0.5 mL of 0.098 M $Cr(NOR)_4$ in CCl_4/C_6H_6 (100:1, v/v) under nitrogen produced no change in the measured shift; this irradiation was enough to fully develop the characteristic orange of the photoproduct; a similar lack of change in susceptibility is also seen in toluene solutions. In order to establish the presence of chloride in the metal photoproduct, all of the volatile organic compounds were removed from a photolyzed solution of II in CCl_4 using trap-to-trap distillation. The remaining solid was mixed with concentrated aqueous KOH and acidified with nitric acid. Silver nitrate was added, and a characteristic precipitate of AgCl formed. A parallel blank sample showed no precipitate.

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Registry No. I, 36333-76-3; II, 36333-78-5; $CrCl_3(THF)_3$, 10170-68-0; $TiCl_4(THF)_2$, 31011-57-1; 1-norbornyllithium, 930-81-4; 1-chloronorbornane, 765-67-3; 1,2′-binorbornyl, 18313-42-3.

EPR Spectra of $V(CO)_5$ and $V(CO)_4$ in a Krypton Matrix[†]

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The free radical carbonyls $V(CO)_4$ and $V(CO)_5$ have been detected by EPR spectroscopy at 20 K in a γ-irradiated sample of $V(CO)_6$ in krypton. $V(CO)_4$ is in a high-spin d^5 configuration ($^6A_1$ in T_d), whereas $V(CO)_5$ appears to have a $^2B_2$ ground state in C_{2v} symmetry (distorted trigonal bipyramid).

Introduction

In recent years we have been studying the EPR spectra of free radical carbonyls centered on transition metals of the first row (V–Ni). Our early experiments involved the dissolution of stable carbonyls, for example, $V(CO)_6$[1] or $Fe(CO)_5$,[2,3] in single crystals of chromium hexacarbonyl followed by generation of paramagnetic derivatives through UV or γ irradiation. This technique was limited by the poor solvent properties of $Cr(CO)_6$, and we were eventually obliged to seek other hosts. Promising results have been obtained with a krypton matrix.[4] Solid krypton is a surprisingly good solvent for transition-metal carbonyls, and EPR spectra observed therein are unusually sharp. On the whole these advantages over $Cr(CO)_6$ outweigh the disadvantages, which are the following: first, liquid helium capability is a prerequisite, and second, the spectra are those of a powder, not a single crystal. The last is a grave disadvantage as it means that principal values of ligand hyperfine interactions are often impossible to obtain, as we shall see. Furthermore, heavy reliance must be placed on computer simulation, a technique which does not always lead to a unique solution.

We had modest success with $V(CO)_6$ dissolved in $Cr(CO)_6$: the spectra of $OV(CO)_{4or5}{}^{2+}$ and $V(CO)_6$ itself were obtained and analyzed.[1] This paper is a discussion of the results obtained from the $V(CO)_6$–krypton system; the spectra of $V(CO)_4$ and $V(CO)_5$ will be described and analyzed.

Experimental Section

The bis(diglyme) complex of $NaV(CO)_6$ was obtained from Alfa Inorganics Inc. and dissolved in sodium-dry tetrahydrofuran. It was then treated with anhydrous H_3PO_4 to liberate the volatile $V(CO)_6$. In order to enrich the $V(CO)_6$ in the isotope ^{13}C, the solution of the vanadium salt was placed under ^{13}CO (Merck, 99.8%) at a pressure of ca. 30 kP in a Pyrex vessel and irradiated with a 100-W high-pressure Hg lamp for 15 h. After the spent CO was removed and replaced twice with fresh ^{13}CO, the solution was treated with H_3PO_4 to liberate the ^{13}C-enriched $V(CO)_6$. An enrichment in excess of 98% was obtained by this method. Appropriate proportions (ca. 1:1000) of $V(CO)_6$ and krypton were mixed in the gas phase and then condensed into a 4-mm o.d. Suprasil sample tube and sealed off at 77 K.

The samples were γ irradiated at 77 K in a 19 000 Ci ^{60}Co γ cell to a total dose of approximately 0.2 Mrad. Alternatively, they were exposed to the full light of a high-pressure Hg–Xe lamp (λ > 254 nm) at 4 K. They were subsequently examined with a Varian E12 EPR spectrometer equipped with an Oxford Instruments ESR 9 liquid-helium cryostat.

Table I. Principal *g* Factors and ^{51}V, ^{13}C Hyperfine Interactions for $V(CO)_5$ in Krypton

axis	*g*	a_V/G	a_C/G
x	1.9877	95.2	2 at 3.3, 2 at 12.8
y	2.0559	35.9	2 at 4.8, 2 at 9.0
z	2.0898	38.2	too weak

Results

The EPR spectrum of $V(CO)_6$ in $Cr(CO)_6$ and other matrices has been discussed elsewhere. Although krypton is known to be a good solvent for transition-metal carbonyls and in general yields splendid EPR spectra, we have never been able to generate a well-resolved spectrum of $V(CO)_6$ in krypton. This fact continues to be a source of considerable frustration and mystification. Suffice to say that unirradiated and irradiated samples of $V(CO)_6$–Kr contained a broad (100 G maximum slope width) derivative-shaped line centered at $g = 2.066$.

The spectrum of irradiated $V(CO)_6$–Kr (natural abundance of ^{13}C) at 20 K is shown in Figure 1a. It is evidently the spectrum of a ^{51}V ($I = {}^7/_2$) centered species having low symmetry, since three distinct manifolds (labeled *x*, *y*, and *z*) of ^{51}V hyperfine structure are apparent. The 24 lines that constitute this spectrum were measured as accurately as possible and, taking $\pm m_I$ pairs, were used to compute principal *g* factors and ^{51}V hyperfine interactions. The usual method of diagonalization of the spin matrix was used.[5] The agreement between the four sets of m_I pairs was ±0.0002 in *g* and ±0.5 G in the ^{51}V hyperfine interaction. The averages of these parameters over the four m_I pairs for *x*, *y*, and *z* are given in Table I.

In Figure 1b a computer simulation obtained by using these parameters is shown.[6] The agreement between the

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