Improved synthesis of (η^5-CpR)M(CO)$_4$ compounds and the Nujol matrix photochemistry of (η^5-C$_5$H$_5$)M(CO)$_4$ and (η^5-C$_9$H$_7$)M(CO)$_4$, where M = Nb and Ta

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Abstract

Improved preparative routes for cyclopentadienyl (Cp) and substituted Cp(CO)$_4$ derivatives of niobium and tantalum and their precursors are described. New compounds are fully characterized by IR, NMR, and elemental analysis. The molecular structures of five compounds were determined: (vinylCp)Nb(CO)$_4$: triclinic, $P\bar{1}$, $a = 6.770(1)$ Å, $b = 6.937(1)$ Å, $c = 12.706(2)$ Å, $\alpha = 90.42(1)°$, $\beta = 91.07(1)°$, $\gamma = 105.560(8)°$, $V = 574.71(12)$ Å^3, $Z = 2$, $R(F) = 2.82$; (acetylCp)Nb(CO)$_4$: monoclinic, $P2_1/c$, $a = 10.316(2)$ Å, $b = 14.490(3)$ Å, $c = 7.957(3)$ Å, $\beta = 94.68(2)°$, $V = 1185.4(4)$ Å^3, $Z = 4$, $R(F) = 2.58$; (Cp)Ta(CO)$_4$: orthorhombic, $Pnma$, $a = 7.756(1)$ Å, $b = 12.159(2)$ Å, $c = 10.580(1)$ Å, $V = 997.7(2)$ Å^3, $Z = 4$, $R(F) = 2.60$; (indenyl)Ta(CO)$_4$: monoclinic, $P2_1/n$, $a = 6.602(2)$ Å, $b = 12.399(1)$ Å, $c = 7.4775(9)$ Å, $\beta = 92.05(2)°$, $V = 611.2(2)$ Å^3, $Z = 2$, $R(F) = 3.05$; and (benzoylCp)Ta(CO)$_4$: monoclinic, $P2_1/c$, $a = 12.552(10)$ Å, $b = 6.5247(2)$ Å, $c = 18.4682(2)$ Å, $\beta = 98.9152(4)°$, $V = 1494.24(5)$ Å^3, $Z = 4$, $RF) = 2.83$ are reported. Photolysis of CpMCO)$_4$ and indenyl)MCO)$_4$, where M = Nb and Ta, in Nujol glass matrices were found to result in loss of one to three CO ligands as a function of the wavelength of the incident light. Annealing or reverse photolysis resulted in reversal of these CO-loss reactions. © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Photochemistry; Niobium; Tantalum

1. Introduction

In contrast to the vast literature of the cyclopentadienyl (Cp) metal carbonyl compounds of most of the transition metals, the paucity of chemistry of the niobium and tantalum compounds is notable. The chief reason for the limited exploration of this class of compounds has been the difficulties associated with their preparation and in the preparation of their precursors. Although King reported the first synthesis of (η^5-C$_5$H$_5$)Nb(CO)$_4$ in 1963 [1], the only high yield route to

be reported since then employs unusually high pressures (4700 psi) and requires 135 h of reaction time [2]. Building upon elegant work by Calderazzo, Pampaloni and their coworkers [3], we have recently reported the synthesis of several previously inaccessible ring-substituted derivatives via Scheme I [4].

In this paper we present the synthesis of additional ring-substituted CpNb and Ta(CO)$_4$ derivatives by this route, and describe the use of Na[M$_2$(CO)$_8$(μ-I)$_3$] as a preferred precursor to these compounds (Scheme Ib). A high yield synthesis of (η^5-C$_5$H$_5$)M(CO)$_4$ from (η^5-C$_5$H$_5$)MCl$_4$ (Scheme II), employing analogous, although somewhat less demanding, conditions to those described by Herrmann is also reported. The photolysis

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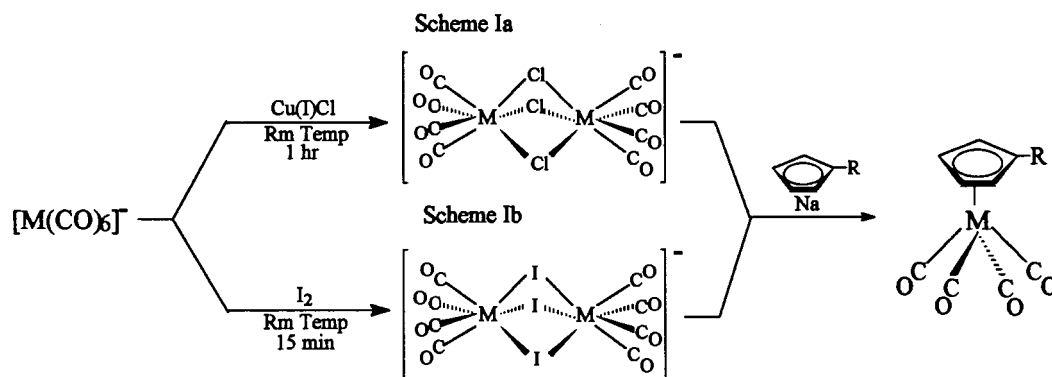
Scheme I. Synthesis of ring-substituted derivatives using $[M(CO)_6]^-$.

2. Synthesis of ring-substituted CpM(CO)$_4$ derivatives

As previously reported, reaction of Na[M(CO)$_6$]·THF, where M = Nb or Ta, with copper(I) chloride or MCl$_5$ in THF under an atmosphere of CO yields Na[M$_2$(CO)$_8$(μ-Cl)$_3$] which is allowed to react without isolation with NaC$_5$H$_4$R or LiC$_5$H$_4$R. After flash filtration of the reaction mixture and removal of solvent, the resulting oily residues are sublimed to yield (η^5-C$_5$H$_4$R)M(CO)$_4$. In many cases the sublimed products were contaminated with an organic oil believed to be bis(Cp) compounds formed by copper coupling of the Cp anions. Repeated sublimations yielded analytically pure products, albeit at the expense of yield.

Removal of the organic oils from the Group V compounds is complicated by the instability of these organometallic compounds to chromatographic conditions. Even brief residence on either neutral alumina or silica gel results in decomposition. In an effort to avoid the side reactions leading to bis(Cp) compounds, we examined the use of alternate reagents for conversion of Na[MCO)$_6$]·THF to the bimetallic, Na[M$_2$(CO)$_8$(μ-X)$_3$] reagents. We have found that the use of a stoichiometric quantity of iodine to Na[M(CO)$_6$]·THF results in formation of Na[M$_2$(CO)$_8$(μ-I)$_3$] as shown by IR. This reagent reacts with NaCpR or LiCpR to yield the corresponding CpM(CO)$_4$ derivatives. Work-up and subsequent sublimation is not complicated by organic impurities resulting in somewhat higher yields with considerably less effort required in purification.

While the use of Na[M$_2$(CO)$_8$(μ-I)$_3$] simplifies the purification of these compounds, the reaction yields remain low to good. This, and the difficulties associated with the synthesis of Na[M(CO)$_6$]·THF, prompted us to examine more direct routes to the desired compounds. Cardoso, Clark and Moorhouse have reported

low pressure reductive carbonylation of (η^5-C$_5$H$_5$)NbCl$_4$ to yield (η^5-C$_5$H$_5$)Nb(CO)$_3$Cl$_2$ [5]. In contrast, under very high pressure conditions, Herrmann has prepared (η^5-C$_5$H$_5$)Nb(CO)$_4$ and its CH$_3$Cp and (CH$_3$)$_5$Cp derivatives. We speculated that intermediate conditions with an appropriate reducing agent and solvent might also yield tetracarbonylated derivatives. Indeed, reaction of (η^5-C$_5$H$_5$)NbCl$_4$, (η^5-C$_5$H$_5$)TaCl$_4$, (η^5-C$_5$H$_4$C$_4$H$_9$)NbCl$_4$, [(η^5-C$_5$H$_4$SiCH$_3$)$_3$]NbCl$_4$ and [(η^5-C$_5$H$_4$SiCH$_3$)$_3$]TaCl$_4$ in pyridine in the presence of Zn/Mg under CO (1600 psi) gave, after work-up and sublimation, good yields of the desired tetracarbonyl derivatives. Scale-up of the reactions to batches of 10 g was readily achieved and further scale-up was only limited by the capacity of the Parr bomb. Since pressures in the range of 1600 psi may be easily achieved in a standard high pressure reaction bomb at typical tank pressures of CO, this preparative route should greatly improve the availability of these compounds. The mono-CpM(CO)$_4$ derivatives were prepared by reaction of MCl$_5$ with RCpTMS and used without purification.

We have been unable to prepare the indenyl, acetyl- or formylCp Group V compounds by this route although preliminary results suggest that the ester derivatives may be prepared in this way.
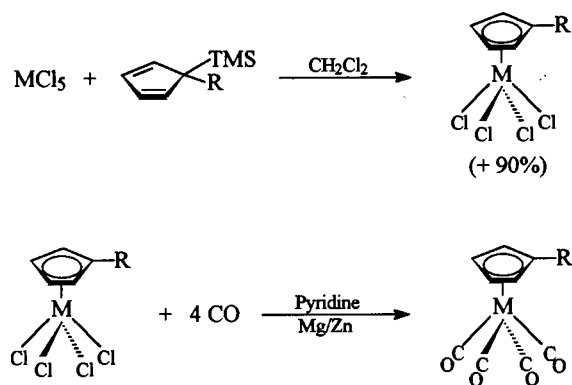

Scheme II. High yield synthesis of (η^5-C$_5$H$_5$)M(CO)$_4$ from (η^5-C$_5$H$_5$)MCl$_4$.

Table 1
IR and ^{93}Nb-NMR data for niobium and tantalum compounds

$(C_5H_4R)M(CO)_4$	IR (CH_2Cl_2) $\nu(CO)$, cm^{-1}		NMR (C_6D_6)
R	Nb	Ta	^{93}Nb
H	2034, 1918	2031, 1910	−2016
CO_2Me	2041, 1929	2037, 1921	−1918
CO_2Et	2038, 1928	2036, 1921	−1919
$C(=O)Me$	2040, 1930	2037, 1922	−1921
$C(=O)C_6H_5$	2040, 1930	2036, 1921	−1904
$C(=O)CH_2C_6H_5$	2040, 1931	2036, 1921	−1917
$C(CH_3)=CH_2$	2033, 1919	2030, 1911	−1953
$CH=CH_2$	2033, 1919		−1946
Indene	2033, 1921	2030, 1912	−1912
$CH_2(CH_2)_2CH_3$	2031, 1915	2028, 1908	−1995
TMS	2031, 1917	2029, 1917	

Attempts to carry out Friedel–Crafts acylation on both $(\eta^5\text{-}C_5H_5)Nb(CO)_4$, $[\eta^5\text{-}C_5H_4Si(CH_3)_3]Nb(CO)_4$, and $(\eta^5\text{-}C_5H_5)Ta(CO)_4$ resulted in complete decomposition of the organometallic species. Lokshin et al. [6] reported that $AlCl_3$ appeared to complex exclusively at the metal in $(\eta^5\text{-}C_5H_5)Nb(CO)_4$, and the metal may also be the preferred point of reaction in acylation reactions as well. The failure of these reactions leaves the reactions described above as the only viable routes to many ring substituted compounds in these series.

2.1. Spectroscopic studies

Carbonyl stretching frequencies of CpM(CO) compounds are known to be sensitive to ring-substituents. The carbonyl stretching frequencies of the Nb and Ta series of compounds, Table 1, are found to increase (relative to R = H) for electron withdrawing groups and decrease for electron donating groups, although the range of values exhibited by each series is too small to carry out meaningful correlations with Hammett substituent constants. Comparison of the carbonyl stretching frequencies between the Nb and Ta series indicates a high degree of correlation between the two, recognizing the limitations imposed by the small range of values.

^{93}Nb-NMR spectra were recorded on the compounds of the series with C_6D_6 as solvent and these values are also reported in Table 1. Comparison of the ^{93}Nb chemical shifts with the carbonyl stretching frequencies indicates that there is no correlation between the chemical shifts and the electron donating or withdrawing effects of the ring substituents. In contrast, Rausch and Graham found good correlations between Hammett substituent parameters or carbonyl stretching frequencies and the ^{103}Rh resonances in a series of $(\eta^5\text{-}C_5H_4R)Rh(CO)_2$ compounds [7]. The reason for the poor correlations in the Nb compounds is not apparent.

Herrman and Biersack [8] have reported the preparation of ^{13}CO and ^{13}C^{18}O enriched $(\eta^5\text{-}C_5H_5)Nb(CO)_4$ via $(\eta^5\text{-}C_5H_5)Nb(CO)_3$THF. Mass spectrometric and infrared spectral studies were conducted on these materials, but there is no mention in this or subsequent papers of ^{13}C-NMR measurements on this enriched compound. For natural abundance ^{13}CO, coupling between the 9/2 spin ^{93}Nb nucleus and the carbonyl carbon results in a broad, ill-resolved resonance in the metal carbonyl region, Fig. 1a. A ^{13}CO enriched sample was prepared by exchange between ^{13}CO and $(\eta^5\text{-}C_5H_5)Nb(CO)_4$ in the dark at room temperature (r.t.) in benzene over a period of several months. IR spectra suggest that on the average slightly more than one CO group had exchanged. The ^{13}C-NMR spectrum of this sample revealed the expected ten-line carbonyl resonance illustrated in Fig. 1b. The ^{13}C–^{93}Nb coupling constant was found to be 222 Hz.

2.2. Molecular structures

The molecular structures of five compounds have been determined. Crystallographic parameters are sum-
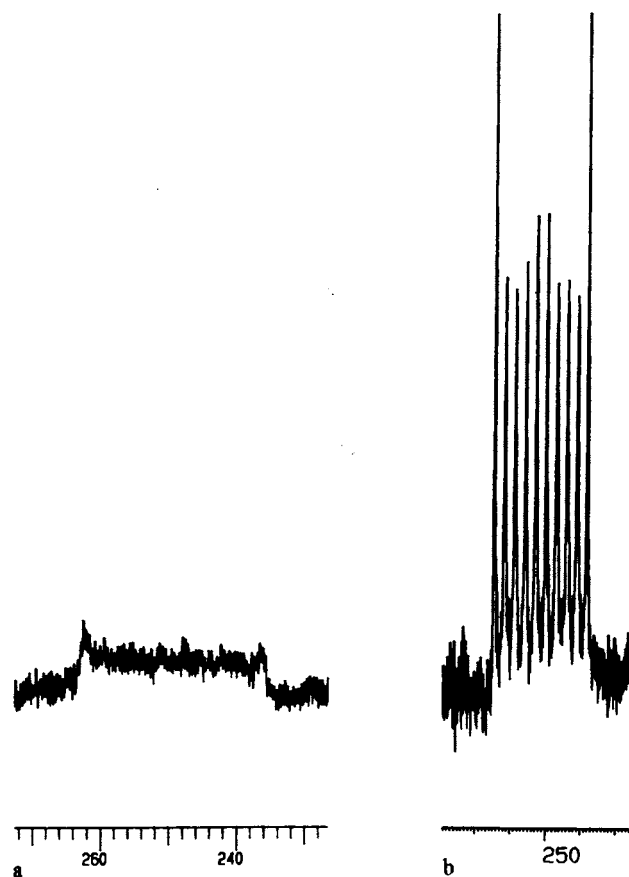

Fig. 1. ^{13}C-NMR of the carbonyl region of (a) $(\eta^5\text{-}C_5H_4CO_2C_2H_5)Nb(CO)_4$ at natural abundance (230000 scans) and b) $(\eta^5\text{-}C_5H_5)Nb(CO)_3$ (^{13}CO) showing ^{13}C–^{93}Nb coupling (264000 scans).

Table 2
Crystallographic data for $(C_5H_4CH=CH_2)Nb(CO)_4$ (**1**), (indenyl)$Ta(CO)_4$ (**2**), $CpTa(CO)_4$ (**3**), $(C_5H_4C(O)Ph)Ta(CO)_4$ (**4**), $(C_5H_4C(O)CH_3)Nb(CO)_4$ (**5**)

	1	2	3	4	5
Formula	$C_{11}H_7NbO_4$	$C_{13}H_7TaO_4$	$C_9H_5TaO_4$	$C_{16}H_9TaO_5$	$C_{11}H_7NbO_5$
Formula weight	296.08	408.14	358.08	462.18	312.08
Space group	$P\bar{1}$	$P2_1/m$	$Pnma$	$P2_1/c$	$P2_1/c$
a (Å)	6.770(1)	6.602(2)	7.756(1)	12.55200(10)	10.316(2)
b (Å)	6.937(1)	12.399(1)	12.159(2)	6.5347(2)	14.490(3)
c (Å)	12.706(2)	7.4775(9)	10.580(1)	18.4682(2)	7.957(3)
α (°)	90.42(1)				
β (°)	91.07(1)	93.05(2)		98.9152(4)	94.68(2)
γ (°)	105.560(8)				
V (Å^3)	574.71(12)	611.2(2)	997.7(2)	1494.24(5)	1185.4(4)
Z	2	2	4	4	4
Crystal color	Orange	Orange	Orange	Orange	Red
Calculated density (g cm^{-3})	1.711	2.219	2.384	2.054	1.749
μ(Mo$-K_\alpha$) (cm^{-1})	10.41	90.00	109.99	73.76	10.20
Temperature (K)	248(2)	243(2)	298(2)	223(2)	243(2)
Radiation	Mo$-K_\alpha$ ($\lambda = 0.71073$ Å)				
$R(F)^a$ (%)	2.82	3.05	2.60	2.83	2.58
$R(wF^2)^a$ %	8.36	8.50	5.94	6.74	6.37

[a] Quantity minimized $= R(wF^2) = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |F_o-F_c|$.

marized in Table 2, while selected bond length and angle data are presented in Tables 3–7. The molecular structures and numbering schemes of these compounds are presented in Figs. 2–6. In all cases, these molecules and those reported previously are found to possess the expected four-legged piano stool geometry. Comparison of metal–carbonyl and carbonyl C–O bond lengths for these compounds reveals no statistically significant differences attributable to the electronic effects of the ring substituents.

The molecular structure of (vinylCp)$Nb(CO)_4$ is, to the best of our knowledge, the first half-sandwich molecular structure of a vinylCp derivative to be reported. As expected, the vinyl group lies in the plane of the Cp ring. The bond length of the C=C is within normal ranges.

2.3. Nujol glass matrix photochemical studies

Rehder and Bechthold [9] have prepared a series of $(\eta^5\text{-}C_5H_5)Nb(CO)_3(PR_3)$ complexes by photolysis of the parent tetracarbonyl in the presence of phosphines and phosphites. Nesmayanov et al. [10] reported the photolysis of the group V compounds with diphenylacetylene to give $(\eta^5\text{-}C_5H_5)M(CO)_2Ph_2C_2)$ and other products. Poliakoff and coworkers [11] have examined the photolysis of the Group V series with H_2, N_2 and silanes in both *n*-heptane (r.t.) and liquid xenon ($-80°C$) using time resolved IR. Hitam and Rest [12] have carried out a detailed photochemical study of $(\eta^5\text{-}C_5H_5)V(CO)_4$ and its ^{13}CO isotopomers in frozen gas matrices at 12 K. A similar photochemical study of ring substituted vanadium compounds including $(\eta^5\text{-}C_9H_7)V(CO)_4$ has

also been reported in frozen gas matrices at 12 K [13]. Poliakoff and coworkers [11] have reported the photolysis of $(\eta^5\text{-}C_5H_5)Ta(CO)_4$ in an argon matrix at 12 K, as well as observation of the $(\eta^5\text{-}C_5H_5)M(CO)_3$ photointermediates by time resolved IR.

Nujol glass matrix photochemical studies in this research were carried out in an apparatus designed by Dr Antony Rest of the University of Southampton. The apparatus and techniques for these photochemical studies have been described previously [14]. Nujol solutions for these studies were prepared in a glove box with minimal background light. Samples were frozen to about 77 K and photolyzed using optical filters to precisely define the wavelengths of light being transmit-

Table 3
Selected bond lengths (Å) and angles (°) for $(C_5H_4CH=CH_2)Nb(CO)_4$

Atoms	Distance	Atoms	Angle
Nb–C(1)	2.094(5)	C(1)–Nb–C(2)	73.7(2)
Nb–C(2)	2.082(4)	C(1)–Nb–C(4)	74.3(2)
Nb–C(3)	2.073(4)	C(2)–Nb–C(3)	73.9(2)
Nb–C(4)	2.093(4)	C(3)–Nb–C(4)	74.01(14)
C(1)–O(1)	1.127(5)	C(1)–Nb–C(3)	117.3(2)
C(2)–O(2)	1.137(5)	C(2)–Nb–C(4)	115.9(2)
C(3)–O(3)	1.144(5)	C(5)–C(10)–C(11)	127.5(6)
C(4)–O(4)	1.134(5)		
Nb–C(5)	2.411(4)		
Nb–C(6)	2.378(4)		
Nb–C(7)	2.395(4)		
Nb–C(8)	2.417(4)		
Nb–C(9)	2.420(4)		
C(5)–C(10)	1.486(7)		
C(10)–C(11)	1.244(7)		

Table 4
Selected bond lengths (Å) and angles (°) for (indenyl)Ta(CO)$_4$

Atoms	Distance	Atoms	Angle
Ta–C(1)	2.064(8)	C(1)–Ta–C(1a)	75.8(5)
Ta–C(2)	2.075(7)	C(1)–Ta–C(2)	73.3(3)
C(1)–O(1)	1.153(10)	C(1a)–Ta–C(2a)	73.3(3)
C(2)–O(2)	1.142(8)	C(2)–Ta–C(2a)	74.2(4)
Ta–C(3)	2.349(10)	C(1)–Ta–C(2a)	117.0(3)
Ta–C(4)	2.380(7)	C(1a)–Ta–C(2)	117.0(3)
Ta–C(5)	2.436(6)		
C(5)–C(6)	1.419(11)		
C(6)–C(7)	1.32(2)		
C(7)–C(7a)	1.43(3)		

Table 6
Selected bond lengths (Å) and angles °) for (C$_5$H$_4$C(O)Ph)Ta(CO)$_4$

Atoms	Distance	Atoms	Angle
Ta–C(1)	2.397(5)	C(6)–Ta–C(7)	73.5(2)
Ta–C(2)	2.398(6)	C(6)–Ta–C(9)	73.1(2)
Ta–C(3)	2.427(5)	C(7)–Ta–C(8)	73.4(2)
Ta–C(4)	2.440(5)	C(8)–Ta–C(9)	73.7(2)
Ta–C(5)	2.431(5)	C(6)–Ta–C(8)	115.4(2)
Ta–C(6)	2.073(6)	C(7)–Ta–C(9)	115.6(2)
Ta–C(7)	2.093(6)	C(1)–C(10)–C(11)	120.3(5)
Ta–C(8)	2.070(6)	C(1)–C(10)–O(10)	119.1(5)
Ta–C(9)	2.075(5)		
C(1)–C(10)	1.507(7)		
C(10)–O(10)	1.221(6)		
C(10)–C(11)	1.514(7)		

ted to the sample. A summary of IR data for compounds and photoproducts is presented in Table 8.

Preliminary observations suggested that compounds in this series are exceptionally light sensitive, an observation that has also been made for the analogous vanadium compounds [15]. Samples of the indenyl compounds had to be prepared in near darkness to avoid photolysis by incident light. In fact, IR spectra recorded on samples of the Ta compound before and after routine UV–vis spectral measurements indicated detectable quantities of photoproducts were formed.

As shown in Fig. 8a and Fig. 11a, both (η^5-C$_5$H$_5$)Nb(CO)$_4$ and (η^5-C$_5$H$_5$)Ta(CO)$_4$ have electronic absorption bands at about 430 and 370 nm and a small band at about 310 nm. In dilute samples, both compounds have a strong band at about 250 nm. Rest et al. assign the corresponding long wavelength bands in (η^5-C$_5$H$_5$)V(CO)$_4$ to d→d and M→π*(CO) transitions, respectively [16]. The short wavelength bands are typically assigned to metal to ligand charge transfer bands although no detailed analysis of the bonding in these compounds is presently available.

Figs. 7 and 10 present IR spectra of (η^5-C$_5$H$_5$)Nb(CO)$_4$ and (η^5-C$_9$H$_7$)Ta(CO)$_4$ in frozen Nujol matrices upon photolysis at various wavelengths and upon annealing. Photolysis of (η^5-C$_5$H$_5$)M(CO)$_4$ and (η^5-C$_9$H$_7$)M(CO)$_4$, M = Nb or Ta, at wavelengths as long as 600 nm (480 < λ < 620 nm) were found to stimulate CO loss as evidenced by difference IR spectra, Fig. 7b and Fig. 10b. These figures show that bands

associated with the carbonyl groups in the starting materials decrease, while a band attributable to 'free' CO (2132 cm^{-1}) and three additional bands consistent with a species of the formula CpM(CO)$_3$ (C$_s$ symmetry) grow in. The band positions for (η^5-C$_5$H$_5$)M(CO)$_3$, where M = Nb and Ta, are within a few cm^{-1} of those reported by Poliakoff et al. [11] in n-heptane (r.t.) and for (η^5-C$_5$H$_5$)Ta(CO)$_3$ in frozen argon (12 K). The observation of carbonyl loss at 600 nm is somewhat puzzling as there are no apparent electronic absorption bands in this region.

Electronic spectra of (η^5-C$_5$H$_5$)M(CO)$_4$, M = Nb or Ta, after photolysis, Fig. 8b and Fig. 11b, and the difference spectra, Figs. 9 and 12, show the bands at 430, 390 and 250 nm (the 250 nm band for Nb is not observed in Fig. 8b due to the high concentration of this sample) to have been bleached while new bands at about 660, 390 and 280 nm grow in. These new bands are associated with the carbonyl-loss photoproducts, (η^5-C$_5$H$_5$)M(CO)$_3$.

Upon photolysis of these Nb and Ta compounds at higher energy (340 < λ < 420 nm), additional bands were observed that may be assigned to the cis and trans dicarbonyl-loss products by analogy to bands assigned

Table 5
Selected bond lengths (Å) and angles (°) for CpTa(CO)$_4$

Atoms	Distance	Atoms	Angle
Ta–C(1)	2.347(11)	C(11)–Ta–C1(1a)	74.9(5)
Ta–C(2)	2.362(8)	C(11)–Ta–C1(2)	74.5(3)
Ta–C(3)	2.357(9)	C(11a)–Ta–C1(2a)	74.5(3)
Ta–C(11)	2.081(9)	C(12)–Ta–C1(2a)	73.4(5)
Ta–C(12)	2.082(10)	C(11)–Ta–C1(2a)	117.4(3)
C(11a)–Ta–C(12)	117.4(3)		

Table 7
Selected bond lengths (Å) and angles (°) for (C$_5$H$_4$C(O)CH$_3$)Nb(CO)$_4$

Atom	Distance	Atoms	Angle
Nb–C(1)	2.370(3)	C(8)–Nb–C(9)	74.88(14)
Nb–C(2)	2.420(3)	C(8)–Nb–C(11)	73.75(13)
Nb–C(3)	2.454(3)	C(9)–Nb–C(10)	74.46(13)
Nb–C(4)	2.425(3)	C(10)–Nb–C(11)	73.67(12)
Nb–C(5)	2.382(3)	C(8)–Nb–C(10)	117.04(12)
Nb–C(8)	2.091(3)	C(9)–Nb–C(11)	117.09(12)
Nb–C(9)	2.096(3)	C(1)–C(6)–C(7)	118.3(3)
Nb–C(10)	2.078(3)	C(1)–C(6)–O(6)	120.0(3)
Nb–C(11)	2.069(3)		
C1)–C(6)	1.488(4)		
C6)–O(6)	1.211(4)		
C6)–C(7)	1.495(4)		
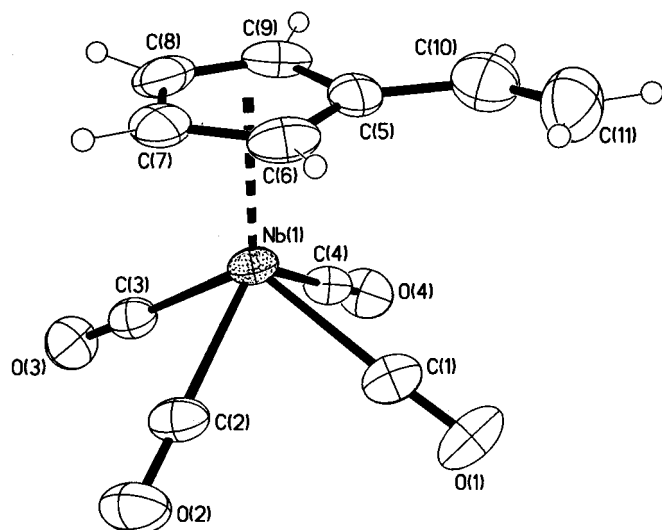
Fig. 2. Molecular structure of $(\eta^5\text{-}C_5H_4CH=CH_2)Nb(CO)_4$.

by Rest to $(\eta^5\text{-}C_5H_5)V(CO)_2$. In the case of $(\eta^5\text{-}C_5H_5)Nb(CO)_4$, the *trans* species is not observed upon photolysis, but appears upon annealing the sample. It is possible that the *cis* species is initially formed in all cases and undergoes either thermal or photochemical conversion to *trans*. Small, but distinct, bands were also observed that correspond to bands assigned by Rest to tricarbonyl-loss fragments [12]. It is likely that Nujol solvates all of the carbonyl-loss products although it is difficult to understand how hydrocarbon solvation might stabilize a formally 12-electron species such as CpM(CO).

As noted above, bands found at about 660 nm in the difference UV–vis spectra are identified with the single-carbonyl loss products, $(\eta^5\text{-}C_5H_5)M(CO)_3$. Photolysis into this band for both the Nb and Ta compounds resulted in recapture of CO by the electron deficient

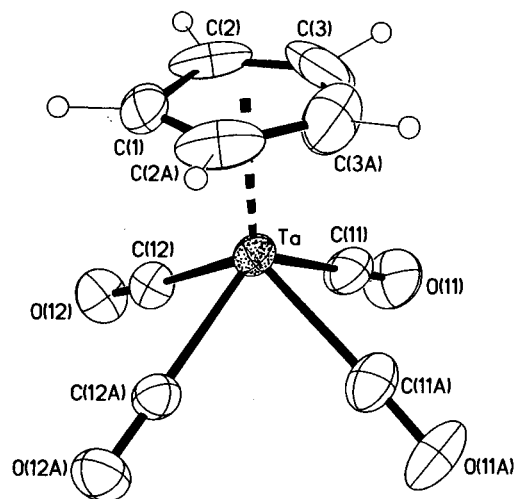Fig. 3. Molecular structure of $(\eta^5\text{-}C_9H_7)Ta(CO)_4$.

Fig. 4. Molecular structure of $(\eta^5\text{-}C_5H_5)Ta(CO)_4$.

species. While photoreversal has been observed by Rest [12], there is no current explanation for how stimulation of an excited band in an isolated metal species prompts ligand capture.

Upon annealing freshly photolyzed samples to 133 K, the bands attributable to 'free' CO, and carbonyl-loss species decayed, while bands of the parent compound grew in. For both $(\eta^5\text{-}C_5H_5)Ta(CO)_4$, and $(\eta^5\text{-}C_9H_7)Ta(CO)_4$ Figs. 10–12 several new bands in the terminal carbonyl region were also observed to grow in upon annealing. We tentatively attribute these bands to a CO capture species in which the η^5-indenyl ring has slipped to its η^3-form. We are initiating solution and supercritical studies of this compound in the presence of a pressure of CO to establish whether such a species may be formed under these conditions. Processes involving what appear to be similar η^5 to η^3 interconversions have been observed by Casey and coworkers for rhenium compounds [17].

The observed photochemical reactions are summarized in Scheme III. Of particular interest in this series of compounds is the ease with which two carbonyl groups can be lost. As the resulting species is formally a 14-electron species, and since highly electron deficient species are known to be important in polymerization catalysis, we are continuing to investigate the photochemistry of these Group V compounds in solution and supercritical fluids such as ethylene.

3. Experimental
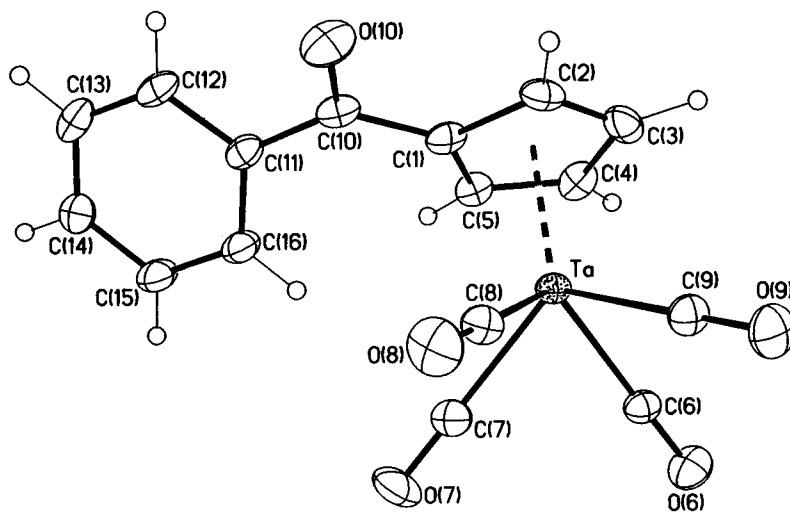
Fig. 5. Molecular structure of $(\eta^5\text{-}C_5H_4CO)C_6H_5)Ta(CO)_4$.

Liquid Carbonic Specialty Gases and used without further purification. ^{13}C-enriched CO (99%) was purchased from Cambridge Isotope Laboratories and used as received. Solvents were dried using appropriate drying agents and distilled under nitrogen.

Column chromatography was carried out using Fisher brand Florisil, silica gel, or Aldrich $\sim$ 150 mesh) neutral alumina. The deactivated silica gel and alumina were placed under vacuum for 24 h at r.t. then stored under nitrogen. Celite was obtained from Fisher Scientific and oven dried prior to use.

NbCl$_5$ and TaCl$_5$ were purchased from Strem Chemicals and were purified by sublimation prior to use. Particularly impure NbCl$_5$ was refluxed in thionyl chloride for 24 h. The solvent was removed under reduced pressure and the yellow solid was sublimed twice to produce pure NbCl$_5$.

Fig. 6. Molecular structure of $(\eta^5\text{-}C_5H_4C((O)CH_3)Nb(CO)_4$.

Proton and carbon NMR spectra were performed on either an IBM NR 300 or a Varian Gemini-300. IR spectra were recorded using either a Digilab Qualimatic FT-IR or a Perkin Elmer FT-IR Spectrum 1000. Mass spectra were obtained using a Vacuum Generators 7070HS GC/MS.

High pressure reactions were carried out in a 300 cm^{-3} Parr series 4560 reactor, equipped with a magnetic stirrer. When necessitated by low tank pressures, the CO pressure in the Parr reactor was boosted using a 10 000 psi, 30 cc, syringe pump, model 62-6-10, from High Pressure Equipment of Eire, PA. Pressure was monitored using a 10 000 psi, temperature compensated, Heise gauge, from Newton Connecticut.

Melting points were determined on a Mel-Temp II apparatus (Laboratory Devices) and are uncorrected. Elemental analysis was performed by Desert Analytics of Tucson, AZ. Li(C$_5$H$_4$CH=CH$_2$) [18], (CH$_3$)$_3$SiC$_5$H$_5$ [19] and [(CH$_3$)$_3$Si]$_2$C$_5$H$_4$ [20] were prepared by literature methods.

3.1. Preparation of $(\eta^5\text{-}C_9H_7)Nb(CO)_4$ via $Na[Nb_2(CO)_8(\mu\text{-}I)_3]$

A 100 cm^3 Schlenk flask was loaded with Na[Nb-(CO)$_6$]·THF (1.2 g, 3.37 mmol) and THF (30 cm^3). The flask was placed under 8 psi of CO and maintained at r.t.. A solution containing iodine (0.85 g, 3.35 mmol) in THF (15 cm^3) was slowly injected into the rapidly stirred mixture. Prompt CO evolution was accompanied by a color change to brown/purple. After the addition was complete the reaction was stirred for 15 min prior to the addition of a THF (25 cm^3) solution of NaC$_9$H$_7$ (0.95 g, 6.88 mmol). Although there was no visible change in the appearance of the mixture, IR established the reaction to be complete within 5 min. The solvent was removed under reduced pressure. The residue was extracted with benzene (3 × 25 cm^3) and the benzene
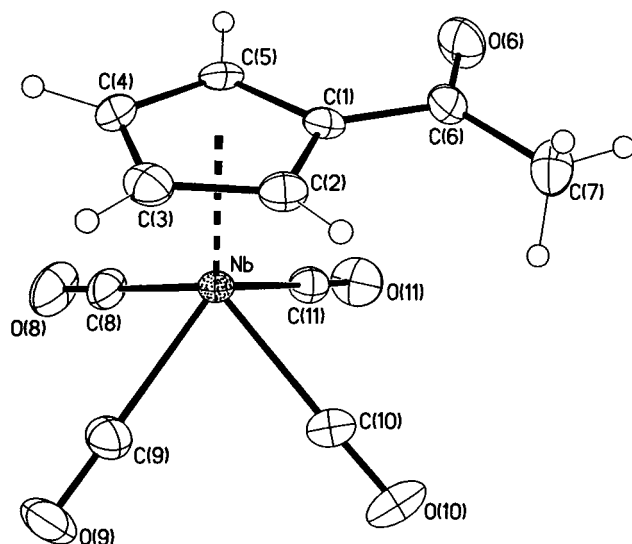
Table 8
IR absorption spectra for niobium and tantalum intermediates[a]

	RM(CO)$_4$	RM(CO)$_3$	RM(CO)$_2$		RM(CO)	(3-C$_9$H$_7$)M(CO)$_4$X
			cis	trans		
CpV(CO)$_4$[b]	2030	1953	1914	1992	1831	2055[c]
	1951	1896	1813	1895		1982
	1930	1857				1946
InV(CO)$_4$[d]	2029	1994				2052[e]
	1957	1917				1978
	1934	1903				
CpNb(CO)$_4$	2034	1982	1898	2006	1844	
	1942	1881	1804	f		
	1927	1871				
InNb(CO)$_4$	2034	1980	1899			
	1947	1883	1809			
	1930	1873				
CpTa(CO)$_4$	2033	1977	1881	1991	1844	2050
	1934	1872	1790	1905		1985
	1918	1859				1951
InTa(CO)$_4$	2032	1975	1887	1996	1846	2049
	1937	1873	1800	1906		1955
	1921	1864				1897

[a] Cp, η^5-C$_5$H$_5$; In, η^5-C$_9$H$_7$; R = Cp or In. [b] In ref. [12], CH$_4$ matrix. [c] Data reported for (3-C$_9$H$_7$)MCO)$_5$ in a CO matrix. [d] In ref. [13], CH$_4$ matrix. [e] Carbonyl stretching frequencies reported for (3-C$_9$H$_7$)M(CO)$_4$(N$_2$) in a nitrogen matrix. The N$_2$ stretching frequency is 2220 cm^{-1}.
[f] Obscured by an overlapping band of another photoproduct, or of low intensity due to low abundance.

extracts filtered through a 3 × 3 cm plug of Celite. The solvent was removed and the residue sublimed to yield a maroon solid. There was no evidence of 1,1′-biindenyl in either the crude product or the sublimed product. Spectral data were identical to those previously reported. Yield: 0.50 g, 46%.

3.2. Preparation of (η^5-C$_5$H$_4$CH=CH$_2$)Nb(CO)$_4$

(η^5-C$_5$H$_4$CH=CH$_2$)Nb(CO)$_4$ was prepared as a deep maroon solid by reaction of LiC$_5$H$_4$CHCH$_2$ with Na[Nb$_2$(CO)$_8\mu$-Cl)$_3$] by the procedure reported previously [4]. The compound appears to be very sensitive to light (even as a solid) and during the first sublimation noticeable discoloration was observed. The material was protected from light during the second sublimation but previous decomposition may account for the particularly poor yield of this compound. Crystals suitable for X-ray analysis were obtained on the second sublimation of the product. Limited sample prevented determination of melting point. IR spectrum (CH$_2$Cl$_2$): 2033 (s), 1919 (vs) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 6.30 m, 1 H, (CH=C), 5.80 br, 2 H, (Cp), 5.45 br, 3 H, Cp and (C=CH$_2$), 5.00 d, 1 H, (C=CH$_2$). ^{13}C-NMR (CDCl$_3$): δ 129.08 (CH=CH$_2$), 113.56 (CH=CH$_2$), 93.26 br, (Cp). ^{93}Nb-NMR (C6D6): δ − 1945.9.0. Anal. Calc. for C$_{11}$H$_7$O$_4$Nb: C, 44.62; H, 2.38. Found: C, 43.86; H, 2.49. Yield: < 5%.

3.3. Preparation of (η^5-C$_5$H$_4$CH$_2$)$_3$(CH$_3$)Ta(CO)$_4$

A 100 cm^3 Schlenk flask was loaded with Na[Ta(CO)$_6$]·THF 1.1 g, 2.48 mmol). After addition of dimethoxyethane (15 cm^3) the flask was placed under an atmosphere of CO (8 psi). In a Schlenk addition funnel a slurry of finely ground TaCl$_5$ (0.68 g, 1.89 mmol) and dimethoxyethane (16 cm^3) under a CO atmosphere was prepared. The TaCl$_5$ slurry was slowly added to the flask containing the hexacarbonyl while the temperature was maintained between − 50 and − 40°C. The flask was allowed to slowly warm to r.t. producing a dark red solution. The solution was stirred at r.t. for 30 min then cooled to 0°C and added to LiC$_5$H$_4$(CH$_2$)$_3$CH$_3$ (0.56 g, 4.41 mmol) in dimethoxyethane (18 cm^3). The resulting solution was heated to 85°C for 14 h. After removal of solvent under reduced pressure, dichloromethane (15 cm^3) was added to give a brown solution which was flash chromatographed through a 12 cm plug of degassed alumina producing a broad orange band. Decomposition and CO evolution was observed while the compound was in contact with the column. The solvent was removed under reduced pressure yielding a small quantity of red oil. IR (CH$_2$Cl$_2$): 2028 (s), 1908 (vs) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 5.7 s, 2 H, (Cp), 5.4 s, 2 H, (Cp), 2.3 m, 2 H, (CH$_2$), 1.4 br m, 4 H, (CH$_2$), 0.9 t, 3 H, (CH$_3$). ^{13}C-NMR (CDCl$_3$): δ 245.4 (CO), 119.6 ipso

(Cp), 94.0 (Cp), 91.4 (Cp), 38.7 (CH_2), 28.8 (CH_2), 22.3 (CH_2), 13.9 (CH_3). Yield: $< 5\%$.

3.4. Preparation of $(CH_3)_3SiC_5H_4(CH_2)_3CH_3$

A 500 cm^3 Schlenk flask was loaded with NaC_5H_5 (12.5 g, 0.142 mol) and ethyl ether (350 cm^3). The flask was placed in an ice bath and 1-bromobutane (19.0 g, 0.139 mol) was slowly injected into the rapidly stirred solution. After 30 min the ice bath was removed and the flask allowed to warm to r.t.. After 20 h the mixture was

allowed to settle and the clear pale yellow layer was filtered into a 500 cm^3 Schlenk flask using a Schlenk filter. The filtrate was cooled in an ice bath and methyl lithium (95 cm^3 of 1.5 M in Et_2O), was slowly added by syringe producing a clear solution. The mixture was stirred for 5 h at r.t.. The flask was again cooled with an ice bath and trimethylsilylchloride (14.5 g, 0.133 mol), was injected into the solution. A pale yellow solution quickly formed and the mixture was allowed to warm to r.t. while stirring overnight. The precipitate was allowed to settle and the solution filtered and concentrated to a bright
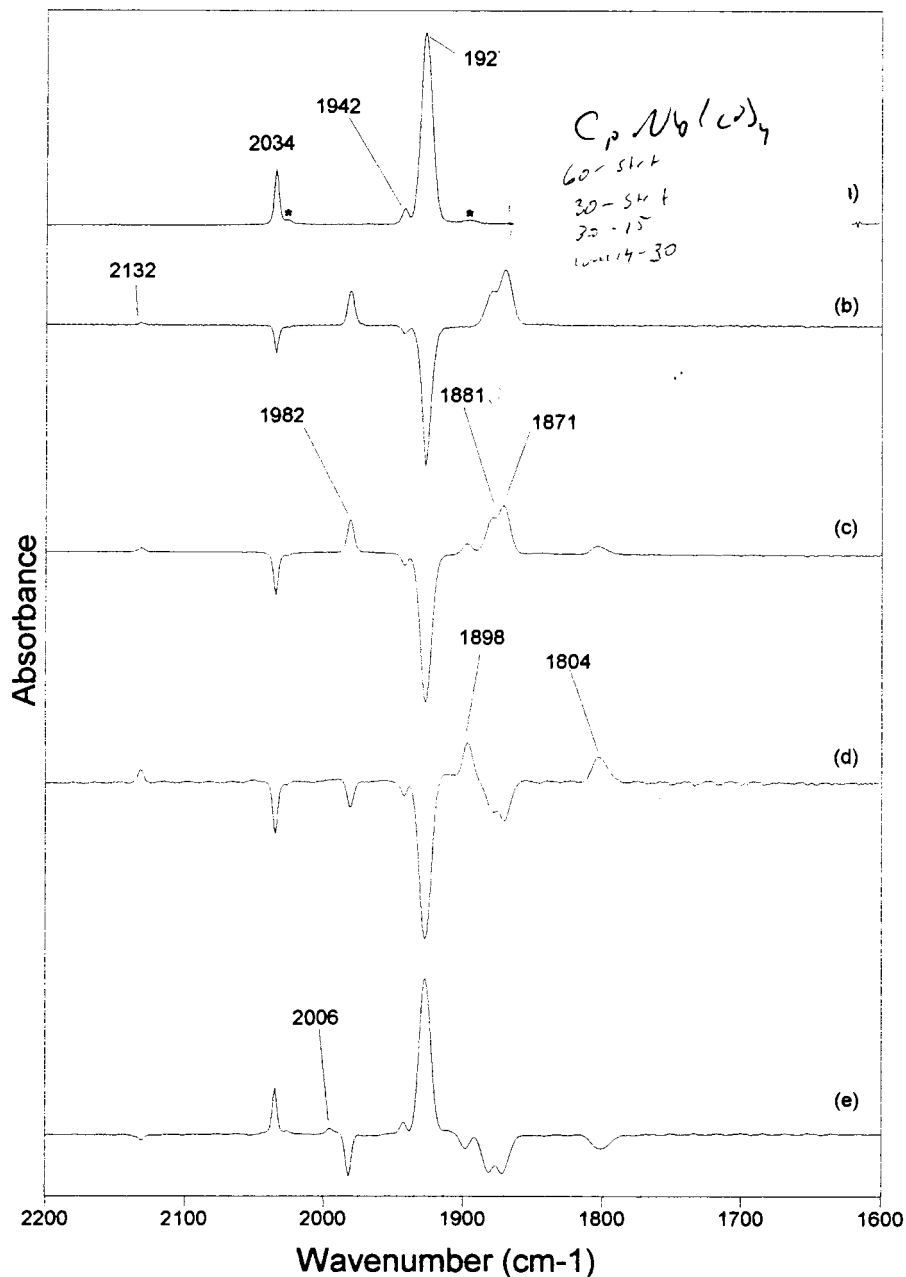
Fig. 7. IR spectra with (η^5-C_5H_5)Nb(CO)$_4$ isolated in a Nujol matrix: (a) starting material, (b) subtraction spectrum, 60 min irradiation at $480 < \lambda < 620$ nm minus starting material, (c) subtraction spectrum, 30 min irradiation at $340 < \lambda < 420$ nm minus starting material, (d) subtraction spectrum, difference between two 15 min periods of irradiation at $340 < \lambda < 420$ nm, (e) subtraction spectrum, anneal to 133 K minus final photolysis. * Arise from (η^5-C_5H_5)Nb(CO)$_3$ (^{13}CO) present in natural abundance.
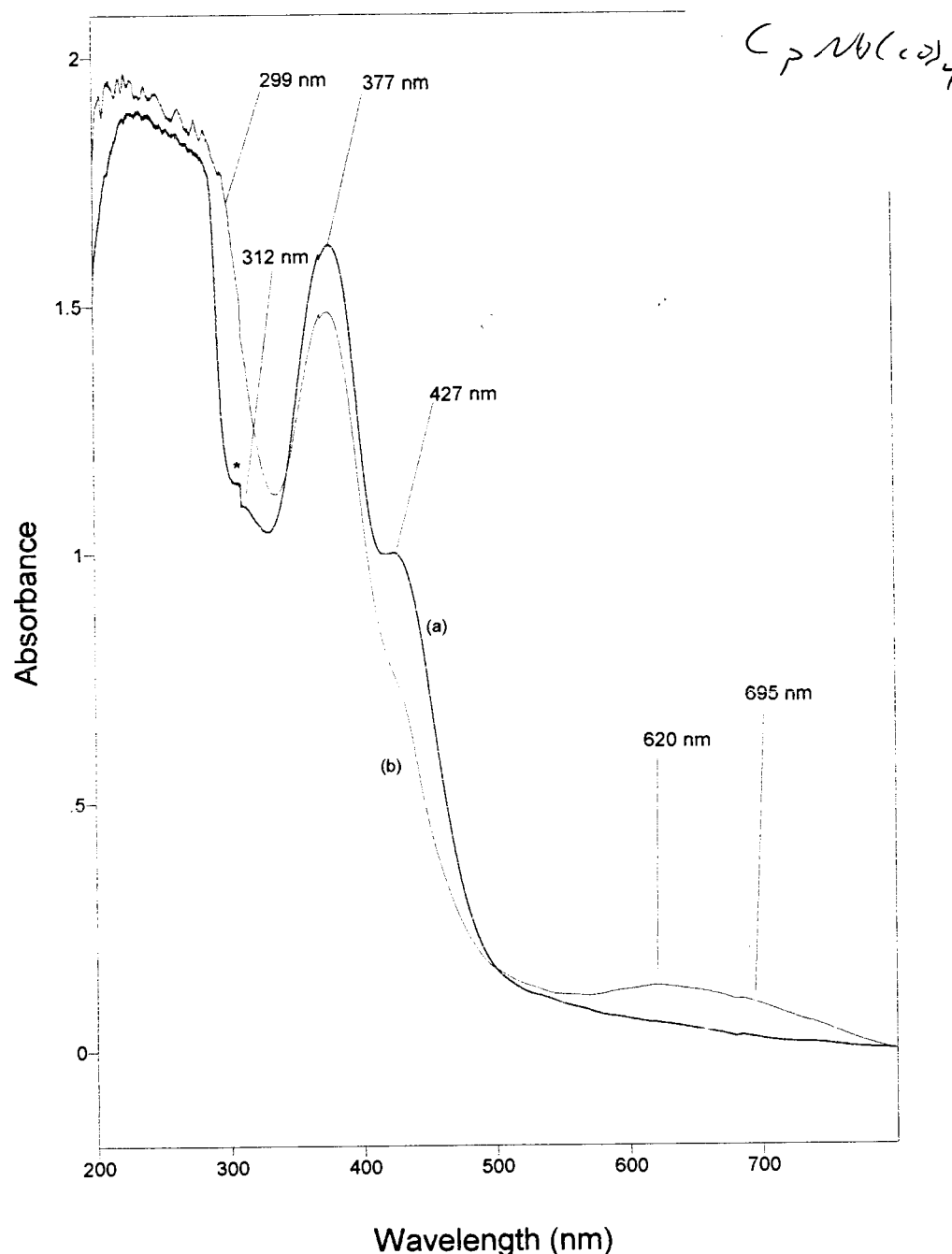
Fig. 8. Electronic absorption spectrum of $(\eta^5\text{-}C_5H_5)Nb(CO)_4$ isolated in a Nujol matrix: (a) starting material, (b) after 60 min irradiation at $480 < \lambda < 620$ nm and 25 min irradiation at $340 < \lambda < 420$ nm. * Irregularity arising from an instrument artifact.

yellow oil. The oil was transferred to a 14/20 short path distillation apparatus and a pale yellow distillate collected (28–34°C at 0.5 torr). ^{1}H-NMR (CDCl$_3$): δ 6.50 (s, 1 H, vinylic), 6.47 (s, 1 H, vinylic), 6.11 (s, 1 H, vinylic), 3.28 (s, 1 H, HCTMS), 2.45 (t, 2 H, $J = 7.3$ Hz, CH$_2$), 1.57 (m, 2 H, CH$_2$), 1.42 (m, 2 H, CH$_2$), 0.96 (t, 3 H, $J = 7.1$ Hz, CH$_3$), 0.00 (s, 9 H, TMS). ^{13}C-NMR (CDCl$_3$): δ 146.0 (ipso), 133.6 (vinylic, CH), 132.3 (vinylic, CH), 126.8 (vinylic CH), 50.8 (HCTMS), 32.2 (CH$_2$), 29.5 (CH$_2$), 22.6 (CH$_2$), 14.0 (CH$_3$), -1.7 (SiCH$_3$)$_3$). Yield: 7.7g, 30%.

3.5. Preparation of $(\eta^5\text{-}C_5H_5)Nb(CO)_4$

A 500 cm^3 Schlenk flask was loaded with finely ground NbCl$_5$ (10.6 g, 39.2 mmol) and CH$_2$Cl$_2$ (400 cm^3). This mixture was rapidly stirred for several hours to produce a fine suspension. To the r.t. mixture (CH$_3$)$_3$SiC$_5$H$_5$ (6.6 g, 47.8 mmol) was added by syringe over 40 min producing an immediate color change to brown/red. After an additional hour stirring was stopped and the fine solid allowed to settle. The brown solution was removed using a filter stick. The residual

solvent was removed under reduced pressure and 11.0 g of fine copper-colored solid was recovered. No further attempt was made to purify the CpNbCl$_4$. The crude tetrachloride was loaded into a 300 cm^3 Parr reactor with magnesium (2.3 g, 94.7 mmol) and zinc (2.3 g, 35.1 mmol). Freshly distilled pyridine (220 cm^3) was transferred into the bomb. Once sealed the bomb was promptly pressurized to 1800 psi and heated to 60°C. Pressure was maintained by frequently recharging with CO. After 86 h the brown solution was poured into a 250 cm^3 Schlenk flask under a flow of nitrogen. The solvent

was removed under reduced pressure using a hot water bath to yield a dark brown solid. The solid was broken up with a spatula and 40 cm^3 of benzene added. After stirring for 30 min, the solution was filtered through a 3×3 cm plug of Celite and the residual solid was washed with fresh benzene (4×25 cm^3). The benzene was removed under reduced pressure to produce an orange/red solid. The solid was sublimed twice to produce 5.1 g of dark maroon solid. IR and NMR data are identical to those previously published. Yield based on the crude (η^5-C$_5$H$_5$)NbCl$_4$ yield: 58%.

Fig. 9. Difference electronic absorption spectrum of (η^5-C$_5$H$_5$)Nb(CO)$_4$ isolated in a Nujol matrix. The difference was taken between the final photolysis 60 min irradiation at $480 < \lambda < 620$ nm and 25 min irradiation at $340 < \lambda < 420$ nm) and the starting material.
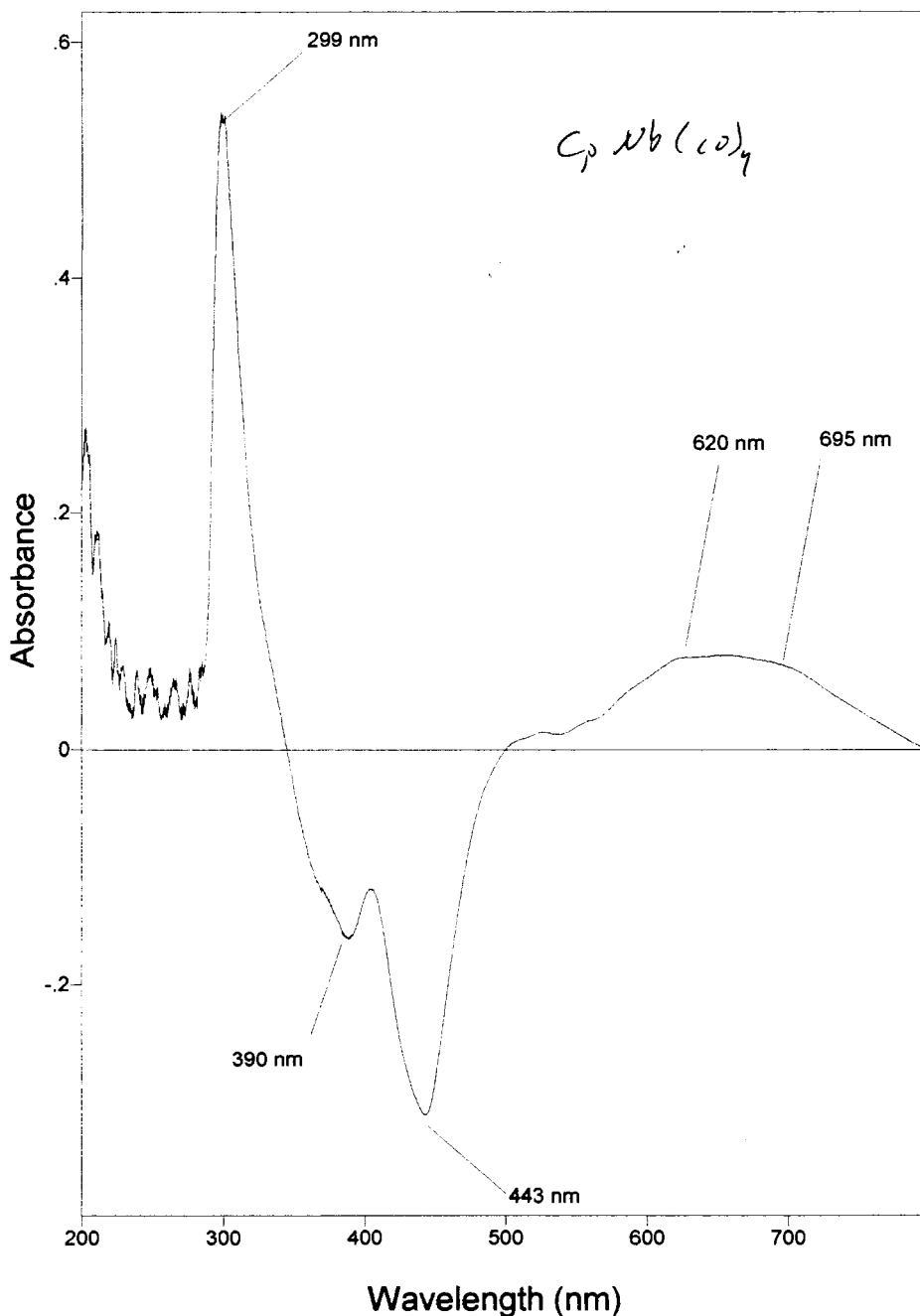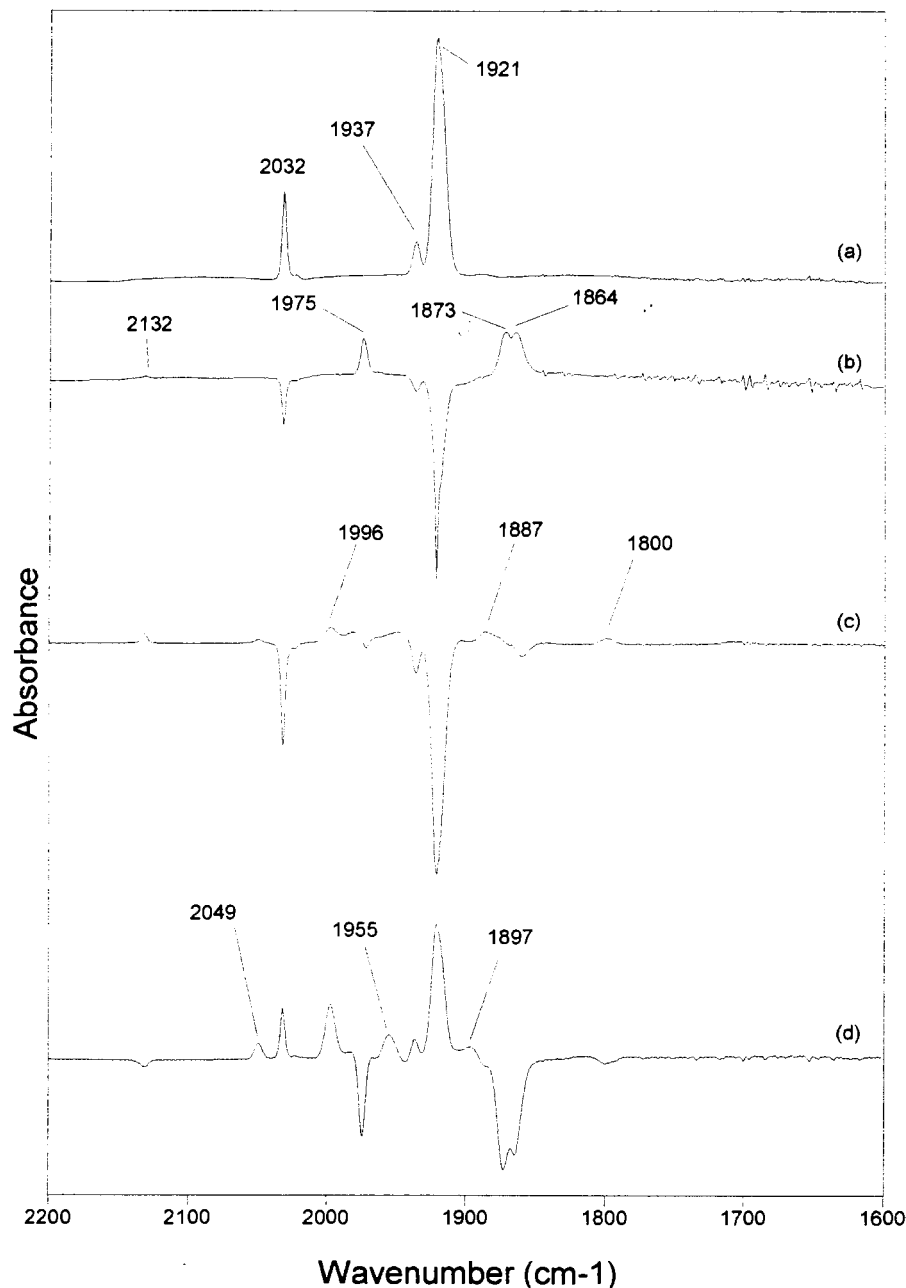
Fig. 10. IR spectra with $(\eta^5\text{-}C_9H_7)Ta(CO)_4$ isolated in a Nujol matrix: (a) starting material, (b) subtraction spectrum, 60 min irradiation at $340 < \lambda < 620$ nm (100 min total at $\lambda > 340$ nm) minus starting material, (c) subtraction spectrum, 20 min irradiation at $\lambda < 285$ nm minus 100 min irradiation at $\lambda > 340$, (d) subtraction spectrum, anneal to 173 K minus 125 min total photolysis at $\lambda > 225$ nm.

This same preparation was attempted with toluene and acetonitrile under identical conditions as those given above but neither produced the desired product. Changing the solvent to THF did produced the $(\eta^5\text{-}C_5H_5)Nb(CO)_4$ which was identified by IR. However, difficulties in purification prohibited the isolation of the compound and no yield could be reported. The above reaction was also conducted under 1.4 atmospheres of CO in pyridine but an IR of the benzene extract showed no metal carbonyls. Increasing the quantity of zinc (3.2 g) while reducing that of magnesium (1.2 g) resulted in a slightly reduced yield (52%).

3.6. Preparation of $(\eta^5\text{-}C_5H_5)Nb(CO)_{4-n}(^{13}CO)_n$

$(\eta^5\text{-}C_5H_5)Nb(CO)_4$ (0.1 g, 0.37 mmol) was loaded into a 60 cm^3 Griffin–Worden tube and benzene (10 cm^3) was added. The solution was freeze/pump/thawed three times to remove nitrogen. The tube was charged to a pressure of 30 psi with ^{13}C-labeled CO. The solution was protected from light and stirred. After 3 months the solution was withdrawn via syringe, placed in a 50 cm^3 Schlenk flask and the solvent removed, producing a orange/red solid. IR Spectrum (CH$_2$Cl$_2$): 2033 (s), 2024 (s), 2016 (s), 1918 (vs), 1897 (vs sh)
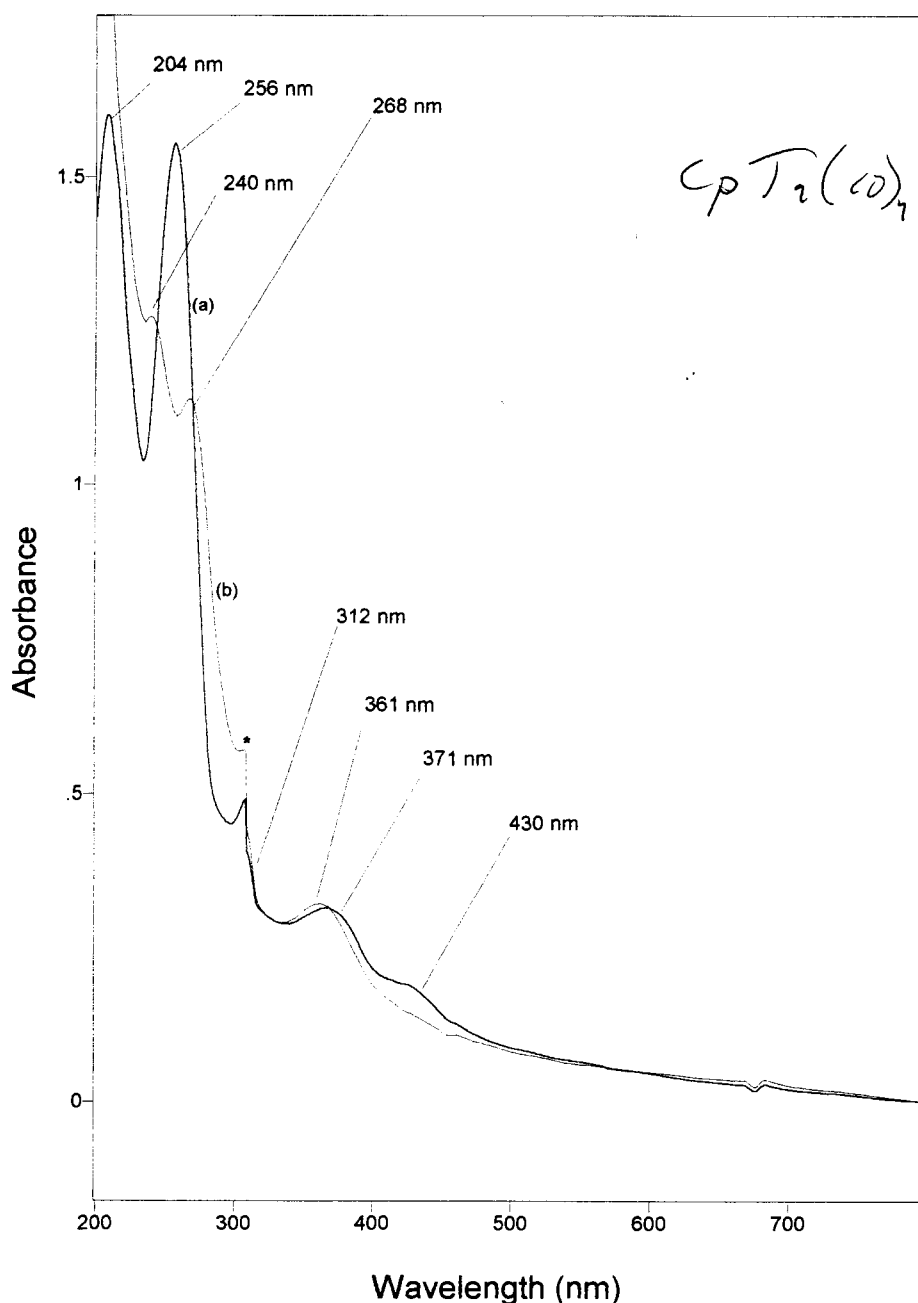
Fig. 11. Electronic absorption spectrum of (η^5-C$_5$H$_5$)Ta(CO)$_4$ isolated in a Nujol matrix: (a) starting material, (b) after 240 min irradiation at $\lambda > 285$ nm . * Irregularity arising from an instrument artifact or an artifact from the cryostat.

cm^{-1}.^{1}H-NMR (CDCl$_3$): δ 5.62–5.55 (br, C$_5$H$_5$). ^{13}C-NMR (CDCl$_3$): δ 251.23 (CO, $J = 222$), 95.24–93.98 (br, C$_5$H$_5$).

3.7. Preparation of (η^5-C$_5$H$_5$)Ta(CO)$_4$

A 500 cm^3 Schlenk flask was loaded with finely ground TaCl$_5$ (12.0 g, 33.5 mol) and of CH$_2$Cl$_2$ (300 cm^3). The mixture was rapidly stirred at r.t. for several hours to produce a fine suspension. CH$_3$)$_3$SiC$_5$H$_5$ (5.4 g, 39.1 mmol) was injected to the TaCl$_5$ suspension over

45 min. There was an immediate color change to orange/brown. The mixture was stirred for several hours at r.t. producing a fine orange precipitate in a brown solution. The flask was placed in the deep freeze ($-$80°C) for several hours and the (η^5-C$_5$H$_5$)TaCl$_4$ was allowed to settle. The brown solution was removed with a filter stick and discarded. The residual solvent was removed from the yellow/orange solid under vacuum. After transferring the flask to the glove box, the crude (η^5-C$_5$H$_5$)TaCl$_4$ (11.2 g) was loaded into the Parr bomb
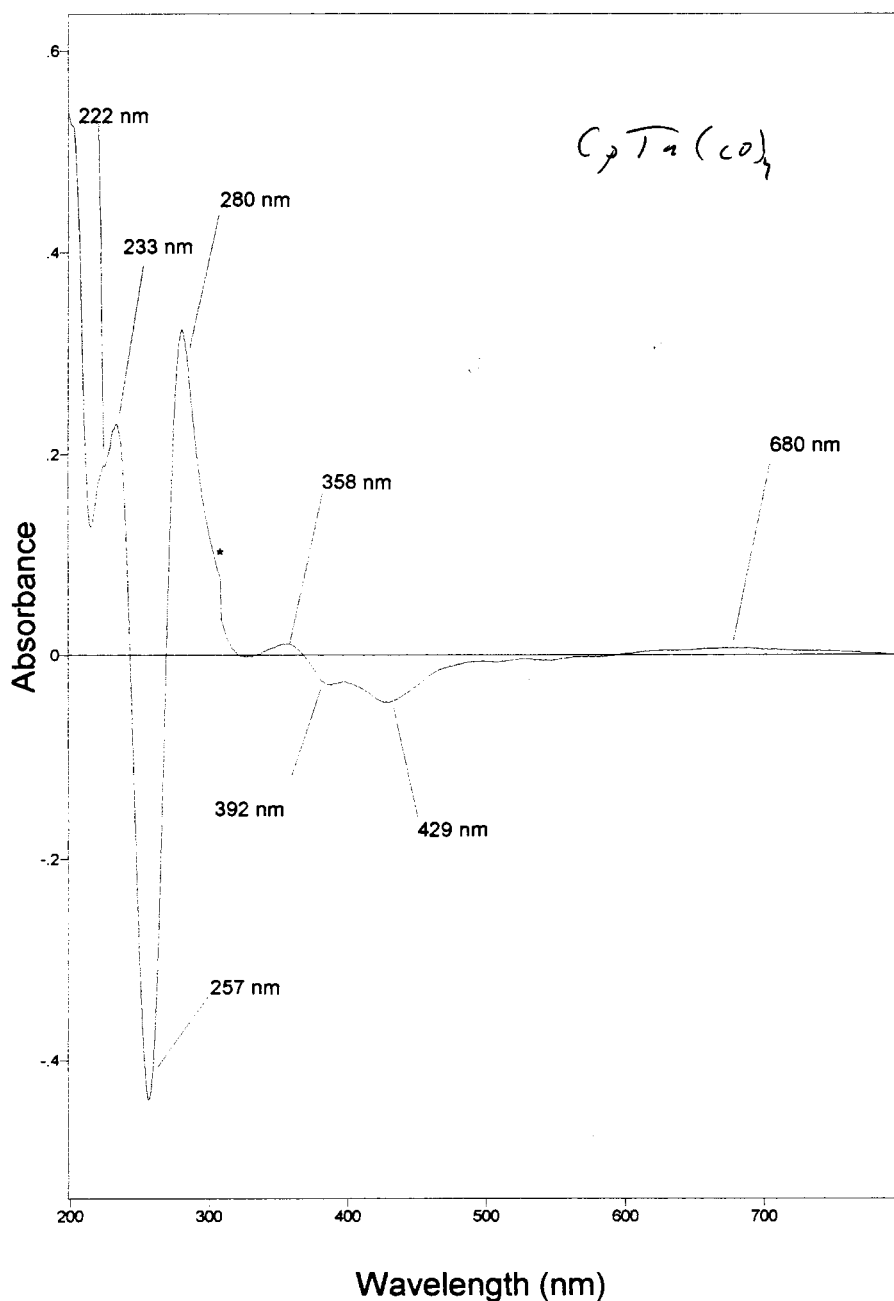
Fig. 12. Difference electronic absorption spectrum of (η^5-C_5H_5)Ta(CO)$_4$ isolated in a Nujol matrix. The difference was taken between the final photolysis (240 min irradiation at $\lambda > 285$ nm) and the starting material. * Irregularity arising from an instrument artifact.

with magnesium (2.1 g, 86.4 mmol) and zinc (2.1 g, 32.1 mmol). Freshly distilled pyridine (220 cm^3) was transferred into the bomb. Upon sealing, the bomb was promptly pressurized with CO to 1600 psi and heated to 60°C. Pressure was maintained by frequently recharging with CO. After 96 h the brown solution was poured into a 250 cm^3 Schlenk flask under a flow of nitrogen. The remaining work up followed that previously outlined in the preparation of (η^5-C_5H_5)Nb(CO)$_4$. (η^5-C_5H_5)Ta(CO)$_4$ was doubly sublimed (85°C, 0.5 Torr) to produce 5.4 g of orange/red crystals. Crystals suitable for X-ray analysis were obtained from the

second sublimation. IR and NMR data were identical to those previously published. Yield (based on the crude CpTaCl$_4$ yield): 52%.

3.8. Preparation of (η^5-$C_5H_4CH_2$)$_3$(CH_3)Nb(CO)$_4$

With some noted exceptions, this compound was prepared in a similar manner as that described for (η^5-C_5H_5)Nb(CO)$_4$, producing a deep maroon oil. Owing to the high solubility of (η^5-$C_5H_4CH_2$)$_3$(CH_3)NbCl$_4$ the compound could not be separated from the reaction solution by filtration as was the case with (η^5-

C$_5$H$_5$)NbCl$_4$. Solvent was removed from the reaction mixture under vacuum and the impure (η^5-C$_5$H$_4$CH$_2$)$_3$(CH$_3$)NbCl$_4$ was loaded directly into the bomb. Once sealed the bomb was promptly pressurized to 1980 psi and heated to 55°C for 19 h. After solvent removal the compound was extracted with several portions of benzene. The resulting red solution was then filtered through a 3 × 3 cm plug of Celite followed by a plug of silica. Removal of the solvent left a brown/red oil. The oil was purified using a very short path distillation apparatus and a hot oil bath (120–136°C at 0.5 torr). The resulting maroon oil is extremely light sensitive and was protected from light. IR (CH$_2$Cl$_2$): 2031 (s), 1915 (vs), cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 5.57 br s, 2 H, (Cp), 5.43 br s, 2 H, (Cp), 2.29 br m, 2 H, (CH$_2$), 1.44 m, 2 H, (CH$_2$), 1.33 m, 2 H, (CH$_2$), 0.89 t, 3 H, J = 7.2 Hz, (CH$_3$). ^{13}C-NMR (CDCl$_3$): δ 120.90 br, *ipso* (Cp), 94.83 br, (Cp), 92.45 br, (Cp), 37.09 (CH$_2$), 28.38 (CH$_2$), 22.27 (CH$_2$), 13.72 (CH$_3$). ^{93}Nb-NMR (C$_6$D$_6$): δ −1995.0. MS (*m/z*): 326 (M$^+$, 6%), 298 (M$^+$−1CO, 2%), 268 (M$^+$−2CO−H$_2$, 9%), 240 (M$^+$−3CO−H$_2$, 16%), 212 (M$^+$−4CO−H$_2$, 36%), 210 (212−H$_2$, 32%),

208 (210−H$_2$, 11%). Exact Mass: Calc. 325.9877; Found, 325.9887. Yield (based on NbCl$_5$): 30%.

3.9. Preparation of [(η^5-C$_5$H$_4$Si(CH$_3$)$_3$]Nb(CO)$_4$

With some noted exceptions, this compound was prepared in a similar manner as that described for (η^5-C$_5$H$_5$)Nb(CO)$_4$, producing a deep maroon solid. As in the case of the butyl derivatives, [η^5-C$_5$H$_4$Si(CH$_3$)$_3$]NbCl$_4$ could not be purified by filtration and the crude material was used directly after solvent removal. The Parr bomb was pressurized to 2150 psi and heated to 50°C for 22 h. [η^5-C$_5$H$_4$Si(CH$_3$)$_3$]Nb(CO)$_4$ and its Ta analog are *extremely* light sensitive and must be stored in the dark to prevent decomposition. M.p. 47°C; dec. 208°C. IR (CH$_2$Cl$_2$): 2031 (s), 1917 (vs), cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 5.70 (br s, 2 H, Cp), 5.55 (br s, 2 H, Cp), 0.18 s, (SiCH$_3$)$_3$). ^{13}C-NMR (CDCl$_3$): δ the *ipso* Cp was not observed, 98.78 (br, Cp), −0.12 (Si(CH$_3$)$_3$). Anal. Calc. for C$_{12}$H$_{13}$O$_4$SiNb: C, 42.12; H, 3.83. Found: C, 41.87; H, 3.68. Yield (based on NbCl$_5$): 52%.

Scheme III. (i) UV–vis irradiation 222 < λ < 620 nm; (ii) UV irradiation 340 < λ < 420 nm, M = Nb, or (η^5-C$_9$H$_7$)Ta(CO)$_4$; (iii) UV irradiation 340 < λ < 420 nm, M = Nb, or (η^5-C$_5$H$_5$)Nb(CO)$_4$ or (η^5-C$_9$H$_7$)Ta(CO)$_4$; (iv) UV irradiation 270 < λ < 290 nm for (η^5-C$_5$H$_5$)Ta(CO)$_4$ or λ > 285 nm for (η^5-C$_9$H$_7$)Ta(CO)$_4$; (v) M = Ta.

3.10. Preparation of [η^5-C$_5$H$_4$ Si(CH$_3$)$_3$]Ta(CO)$_4$

With some noted exceptions, this compound was prepared in a similar manner as that described for (η^5-C$_5$H$_5$)Ta(CO)$_4$, producing a highly light-sensitive bright orange solid. [η^5-C$_5$H$_4$Si(CH$_3$)$_3$]TaCl$_4$ could not be separated from its reaction mixture so the crude material was used after removal of solvent. The Parr bomb was pressurized to 1970 psi and heated to 55°C for 63 h. M.p. 59°C; dec. 225°C. IR (CH$_2$Cl$_2$): 2029 (s), 1909 (vs), cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 5.73 s, 2 H, (Cp), 5.55 s, 2 H, (Cp), 0.20 s, (Si(CH$_3$)$_3$). ^{13}C-NMR (CDCl$_3$): δ 244.62 (CO), 105.05 *ipso* (Cp), 98.44 (Cp), 97.79 (Cp), −0.12 (Si(CH$_3$)$_3$). Anal. Calc. for C$_{12}$H$_{13}$O$_4$SiTa: C, 33.50 H, 3.05. Found: C, 33.20; H, 2.90. MS (*m/z*): 430 (M$^+$, 18%), 402 (M$^+$−1CO, 9%), 387 (402−Me, 6%), 374 (M$^+$−2CO, 7%), 359 (374−Me, 5%), 346 (M$^+$−3CO, 42%), 318 (M$^+$−4CO, 100%), 246 (M$^+$−4CO−TMS, 9%). Exact Mass: Calc. 430.0036; Found, 430.0047. Yield (based on TaCl$_5$): 42%.

3.11. Crystallographic structure determination

The single crystal X-ray diffraction experiments were performed on a Siemens P4 diffractometer for **1**–**3** and **5**, and on a Siemens P4/CCD diffractometer for **4**.

The systematic absences in the diffraction data were consistent for the reported space group. For **2**, either of the monoclinic space groups $P2_1$ and $P2_1/m$ was indicated; for **3**, either of the orthorhombic space groups $Pna2_1$ and $Pnma$ was indicated; in both cases the latter centrosymmetric space groups were preferred based on the chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix least-squares procedures. The data were corrected for absorption for **2**, **4** and **5**. The absorption corrections were not required for **1** and **3** because the variation in the integrated Ψ-scan intensities was < 10%; the empirical absorption corrections for **2** and **4** were applied by using the program DIFABS; the semi-empirical absorption correction data for **5** were collected by the Ψ-scan technique. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. In **2**, atoms Ta, C(3), and H(3A) reside in a mirror plane. In **3**, atoms (Ta, C1), and H(1A) reside in a mirror plane. In the case of **2**, the final difference map contained a single large peak (ca. 1.02 eÅ^3) in a chemically unreasonable position as its only prominent feature. The final difference maps in the cases of **1** and **3**–**5** were featureless.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.03) program

library [21]. Program DIFABS is described by Walker and Stuart [22].

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