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METHYL AND ACETYL COMPLEXES OF CHROMIUM AND TUNGSTEN. OBSERVATIONS ON METAL—CARBON BOND STRENGTH VARIATIONS IN THE CHROMIUM TRIAD

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Summary

The complexes *trans*-(h^5-C_5H_5)M(CO)$_2$(L)COCH$_3$ [M = Cr, L = P(C_6H_5)$_3$, P(*p*-$CH_3OC_6H_4$)$_3$, P(C_6H_5)(CH_3)$_2$; M = W, L = P(C_6H_5)$_3$, P(*p*-$CH_3OC_6H_4$)$_3$, P(C_6H_5)(CH_3)$_2$, P(n-C_4H_9)$_3$] have been synthesized by the direct reaction of h^5-C_5H_5M(CO)$_3$CH$_3$ and the appropriate phosphine in acetonitrile solution. The structures of the subject compounds have been assigned on the basis of proton NMR and IR spectroscopy. Bonding and electron distribution are compared to the isostructural molybdenum complexes on the basis of the spectral data obtained. Both the initial reactions of the h^5-C_5H_5M(CO)$_3$CH$_3$ complexes with phosphorus ligands and ease of decarbonylation of the acetyl products h^5-C_5H_5M(CO)$_2$(L)COCH$_3$ are consistent with the generally observed sequence of metal—carbon bond strengths in the triad, W $\gg$ Mo $\gg$ Cr. Mass spectral data are reported for the tungsten complexes containing tri-n-butyl- and phenyldimethyl-phosphine and the reactions of the subject complexes with iodine are discussed.

Introduction

The so-called "carbon monoxide insertion" reactions of h^5-C_5H_5Mo(CO)$_3$R complexes (R = a σ-bonded organic group) have been the subject of considerable interest in recent years [1,2]. Related reactions of chromium and tungsten analogues have not been studied in detail, due in part to the thermal instability of the chromium complexes and the relatively great inertness of h^5-C_5H_5W(CO)$_3$CH$_3$ [1,2]. We recently reported the first well-defined examples of the carbon monoxide insertion reaction of h^5-C_5H_5Cr(CO)$_3$CH$_3$ [3] and present herein the details of this work. In addition, we wish to report the first general, convenient synthesis of the tungsten acetyl complexes h^5-C_5H_5W(CO)$_2$(L)COCH$_3$ (L = a tertiary phosphine). The availability of these complexes allows for the first time a discussion of the structure, bonding and reactivity of a homologous series of Group VI compounds of the general formula h^5-$C_5H_5M(CO)_2(L)X$ (L = a trivalent phosphorus ligand, X = a σ-bonded group).

Experimental

All operations were conducted under nitrogen or argon atmospheres, including admission of argon to evacuated flasks. Acetonitrile was distilled from phosphorus pentoxide under argon and stored over Linde 4A Molecular Sieves. Other solvents were dried by standard methods and also stored under dry, oxygen-free conditions. Metal hexacarbonyls were generous gifts of Climax Molybdenum Co. and were used as received. Phosphorus ligands were purchased from Strem Chemical Co. and Aldrich Chemical Co. The complexes h^5-$C_5H_5Cr(CO)_3CH_3$ [4] and h^5-$C_5H_5W(CO)_3CH_3$ [5] were prepared by standard literature methods.

Elemental analyses (Table 1) were conducted by Galbraith Microanalytical Laboratories, Knoxville, Tennessee. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer using carbon tetrachloride or cyclohexane solvents with matched 0.1 mm potassium bromide cells. Spectra were calibrated with 1944.0 and 1601.4 cm^{-1} bands of polystyrene and are accurate to ± 2 cm^{-1}. These data are collected in Table 2. NMR spectra were obtained on a Varian Associates T-60 instrument using deuteriochloroform or acetone-d_6 solvents and tetramethylsilane as internal standard. These data are given in Table 3, along with values for the corresponding molybdenum complexes. Mass spectra were obtained on an AEI MS-1201B spectrometer at an ionizing voltage of 70eV. Samples were introduced directly into the probe. Typical examples of the synthetic procedures utilized are given below.

Synthesis of h^5-$C_5H_5Cr(CO)_2[P(C_6H_5)_3]COCH_3$

Chromium hexacarbonyl (3.3 g, 15 mmoles) and sodium cyclopentadienide [7.3 g of 18% THF solution (Columbia), 15 mmoles] were refluxed in 250 ml THF under argon for 36 hours. The mixture was cooled to 0° and 2.2 g methyl iodide (15 mmoles) added dropwise. Stirring was continued for two hours at room temperature and solvent removed via rotary evaporator at room temperature. No attempt was made to isolate the very unstable [4] h^5-C_5H_5-$Cr(CO)_3CH_3$. The residue was extracted with acetonitrile (total 100 ml) and treated with 3.9 g of triphenylphosphine (15 mmoles) and the mixture stirred at room temperature for two hours. Solvent was removed via rotary evaporator at room temperature and the residue extracted with chloroform. Chromatography on Woelm Neutral Alumina (Grade III) with 1/1 chloroform-hexane afforded a small yellow band which was collected but could not be isolated. A second yellow band, eluted with pure chloroform, was evaporated to dryness and recrystallized from chloroform-heptane to afford h^5-$C_5H_5Cr(CO)_2[P(C_6H_5)_3]COCH_3$, 3.1 g, 43% yield based on $Cr(CO)_6$. The other chromium acetyls (Table 1) were prepared by identical procedures.

Synthesis of h^5*-*$C_5H_5W(CO)_2[P(n\text{-}C_4H_9)_3]COCH_3$

To a three necked flask fitted with argon inlet and reflux condenser were charged 100 ml dry acetonitrile, 1.0 g h^5-$C_5H_5W(CO)_3CH_3$ and 0.8 g tri-n-butylphosphine (3.9 mmoles). The solution was heated at reflux under argon with magnetic stirring for 90 hours, at which time the NMR spectrum of an aliquot of the solution showed 60% conversion of starting material to h^5-$C_5H_5W(CO)_2[P(n\text{-}C_4H_9)_3]COCH_3$ and a trace of h^5-$C_5H_5W(CO)_2[P(n\text{-}C_4H_9)_3]CH_3$. Acetonitrile was removed by rotary evaporator and the residue taken up in dichloromethane and chromatographed on Woelm Neutral Alumina (Grade III). Two yellow bands were developed, the first being starting material and a trace of h^5-$C_5H_5W(CO)_2[P(n\text{-}C_4H_9)_3]CH_3$ which was not isolated in pure form. Total weight of this first fraction was 0.45 g. The second band was eluted with 1/3 methanol-dichloromethane. Removal of solvent at reduced pressure and two recrystallizations from hexane at − 78° afforded 0.26 g of h^5-$C_5H_5W(CO)_2[P(n\text{-}C_4H_9)_3]COCH_3$, 27% based on converted h^5-$C_5H_5W(CO)_3CH_3$. The other tungsten acetyls (Table 1) were prepared similarly, typical reaction times in refluxing acetonitrile being 4 - 6 days.

Reactions of h^5*-*$C_5H_5M(CO)_2[P(C_6H_5)_3]COCH_3$ *complexes with iodine*

To 10 mls of a chloroform solution of h^5-$C_5H_5W(CO)_2[P(C_6H_5)_3]COCH_3$ (0.13 g. 0.2 mmoles) was added 0.05 g (0.2 mmoles) of iodine. The reaction mixture was stirred four hours at room temperature. Solvent was removed by rotary evaporator, the residue dissolved in chloroform and chromatographed on Woelm Neutral Alumina. Development with 1/1 hexane-chloroform afforded a single red band. Solvent was removed and the product recrystallized from chloroform-pentane to afford 0.10 g, 66% yield of a mixture of *cis*- and *trans*-(h^5-C_5H_5)$W(CO)_2[P(C_6H_5)_3]I$. (Analysis Found: C, 44.45; H, 3.12; P, 4.76. $C_{25}H_{20}IO_2PW$ calcd.: C, 43.26; H, 2.90; P, 4.46%. The complex has m.p. 183 - 185° (uncorrected) and shows strong IR CO stretching frequencies at 1876 and 1960 cm^{-1}. The proton NMR spectrum ($CDCl_3$, 37°) shows the expected phenyl resonance centered at δ 7.55 ppm, a singlet at δ 5.47 ppm (*cis*-isomer) and a doublet (J(PH) 2.0 Hz) at δ 5.15 ppm (*trans*-isomer). Integration of the phenyl resonance and total h^5-C_5H_5 resonances gave the expected 15/5 ratio. Attempts to synthesize the analogous chromium complex led only to decomposition of the starting chromium acetyl complex.

Kinetic measurements of the reactions of h^5*-*$C_5H_5W(CO)_3CH_3$ *with triphenyl- and tri-n-butylphosphine*

Purification of materials. The tungsten complex, h^5-$C_5H_5W(CO)_3CH_3$, was purified by sublimation (80°/0.1 mm). Triphenylphosphine and tri-n-butylphosphine (Aldrich Chemical Co.) were used as obtained. The reaction solvent, acetonitrile, was purified by distillation under argon from phosphorus pentoxide and stored over Linde 4A molecular sieves under argon atmosphere until use.

Determination of rate constants. In all cases the concentration of the phosphine ligand was at least 7.5 times the concentration of h^5-$C_5H_5W(CO)_3CH_3$ and was assumed to remain constant throughout the course of the reaction. The ratio of the concentration of phosphine used to the concentration of

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR $(h^5\text{-}C_5H_5)M(CO)_2(L)COCH_3$ COMPLEXES

M	L	m.p.[a] (°C)	yield (%)	Analysis calcd. (found)		
				C	H	P
Cr	$P(C_6H_5)_3$	118 - 120	43[c]	67,78 (67,39)	5,44 (4.79)	6.48 (6.59)
Cr	$P(p\text{-}CH_3OC_6H_4)_3$	132 - 133	21[c]	63,38 (62,73)	5,10 (5,12)	5.46 (5.34)
Cr	$P(C_6H_5)(CH_3)_2$	74 - 75	14[c]	57,63 (57,33)	5,37 (5,35)	8.76 (8.85)
W	$P(C_6H_5)_3$	184.5 - 186	40[d]	53,15 (53,04)	3,80 (3,80)	5.08 (5.01)
W	$P(p\text{-}CH_3OC_6H_4)_3$	182 - 185	36[d]	51,45 (51,40)	4.17 (4.18)	4.42 (4.37)
W	$P(C_6H_5)(CH_3)_2$	140 - 141	60[d]	42,00 (42,32)	3,94 (4.01)	6.37 (6.38)
W	$P(n\text{-}C_4H_9)_3$	109 - 112	27[d]	45,82 (45,65)	6.41 (6.34)	5.63 (5.63)

[a] Determined on a Thomas-Hoover Capillary Melting Point apparatus and are uncorrected. [b] Galbraith Microanalytical Laboratories. [c] Yield basis, $Cr(CO)_6$. [d] Yield basis, converted $CpW(CO)_3CH_3$.

h^5-$C_5H_5W(CO)_3CH_3$ was varied from 7.5/1 to 20/1. The progress of the reaction was monitored by integration of the appropriate cyclopentadienyl proton resonances in the NMR of starting material and products, h^5-$C_5H_5W(CO)_2$-$(L)COCH_3$ and h^5-$C_5H_5W(CO)_2(L)CH_3$. (Only trace amounts of the latter product were observed.) In all cases the reaction was allowed to proceed through at least 1.5 half-lives.

A linear least squares fit of the data (concentration of h^5-$C_5H_5W(CO)_3$-CH_3 vs. reaction time) yielded a pseudo-first-order rate constant, k_{obsd}, for the insertion reaction. No dependence on either the nature of the ligand or its concentration was observed, implying a rate expression of the form rate = $k[h^5\text{-}C_5H_5W(CO)_3CH_3]$. The value of k_{obsd} was found to be $3.5 \pm 0.5 \times 10^{-6}$ sec^{-1}. Correlation coefficients greater than 0.99 were obtained from the least squares plot for each run. A typical run is described below.

Reaction of h^5-$C_5H_5W(CO)_3CH_3$ with $P(C_6H_5)_3$. Into a two necked round bottom flask equipped with magnetic stirrer, reflux condenser, and argon inlet was added $P(C_6H_5)_3$ (7.6068 g, 0.029 mol) and 100 ml CH_3CN. The solution was allowed to equilibrate in an oil bath to 82° (refluxing CH_3CN) and h^5-$C_5H_5W(CO)_3CH_3$ (1.0092 g., 0.0029 mol) added. Five ml aliquots were syringed from the reaction solution at approximate 12 h intervals. Acetonitrile was removed via rotary evaporator, the remaining yellow solid dissolved in NMR-grade $CDCl_3$, and a proton-NMR spectrum recorded.

Results and Discussion

The complexes h^5-$C_5H_5M(CO)_3CH_3$ (M = Cr,W) react with tertiary phosphines in acetonitrile to yield substituted acetyl complexes according to eqn. 1.

$$(h^5\text{-}C_5H_5)M(CO)_3CH_3 + PR_3 \rightarrow \textit{trans}\text{-}(h^5\text{-}C_5H_5)M(CO)_2(PR_3)COCH_3 \qquad (1)$$

Although this general reaction scheme has been known for some time for M = Mo [6 - 10], the chromium and tungsten alkyls have not been studied in detail. As we reported previously [3] the chromium acetyl complexes are obtained in moderate yields by utilizing the extremely unstable [4] h^5-C_5H_5-$Cr(CO)_3CH_3$ generated in situ from $Na[h^5\text{-}C_5H_5Cr(CO)_3]$ and methyl iodide. The products are extremely air sensitive in solution but in the solid state may be stored under argon for several months at 0°. The tungsten complexes are considerably more stable, both thermally and oxidatively, than either the chromium or molybdenum analogues. Physical and analytical data for the new complexes h^5-$C_5H_5M(CO)_2(L)COCH_3$ [M = Cr,L = $P(C_6H_5)_3$, $P(p\text{-}CH_3OC_6H_4)_3$, $P(C_6H_5)(CH_3)_2$; M = W,L = $P(C_6H_5)_3$, $P(p\text{-}CH_3OC_6H_4)_3$, $P(C_6H_5)(CH_3)_2$, $P(n\text{-}C_4H_9)_3$] are presented in Table 1.

The relative ease of formation of the chromium, molybdenum and tungsten acetyls (eqn. 1) serves as an interesting example of the metal—carbon bond strength variations which occur in the chromium triad [1,11,12]. The chromium [3] and molybdenum acetyls [8 - 10] are formed at room temperature in acetonitrile solvent, but we observed no reaction for the tungsten complex h^5-$C_5H_5W(CO)_3CH_3$ under these conditions*. Even in refluxing acetonitrile

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* The complex h^5-$C_5H_5W(CO)_2[P(C_2H_5)_3]COCH_3$ is reported [13] to result from the reaction of h^5-$C_5H_5W(CO)_3CH_3$ with neat triethylphosphine at 50°. Traces of h^5-$C_5H_5W(CO)_2[P(C_6H_5)_3]$-$COCH_3$ have been isolated from the reaction of h^5-$C_5H_5W(CO)_3COCH_3$ with $P(C_6H_5)_3$ in tetrahydrofuran [14].

(82°) the tungsten reaction is very slow ($k = 3.5 \pm 0.5 \times 10^{-6} sec^{-1}$) relative to the corresponding insertion of the molybdenum complex [8] at 30° ($k = 5 \pm 1 \times 10^{-4} sec^{-1}$). No kinetic data are available for h^5-$C_5H_5Cr(CO)_3CH_3$ due to its thermal and oxidative instability, but based on our qualitative observations the rates appear to be comparable with those of the molybdenum complex. If, as is generally believed [2,7,8], the rate determining step in these reactions is migration of the methyl group to a terminal CO forming the unsaturated h^5-$C_5H_5M(CO)_2COCH_3$, thse data reflect a decrease in metal—carbon bond strengths W $\gg$ Mo $\gg$ Cr. The rate constants for the tungsten insertion reactions (eqn. 1, M = W) are independent of both the phosphine utilized and its concentration, again paralleling the behavior exhibited by h^5-$C_5H_5Mo(CO)_3CH_3$ in donor solvents [7,8,15] and indicating that the reaction mechanism is independent of the metal in the starting complex.

Additional chemical evidence concerning the relatively great strength of the tungsten—carbon bond is the reluctance of the tungsten acetyls to undergo thermal decarbonylation (eqn. 2) to the corresponding σ-methyl complex.

$$h^5\text{-}C_5H_5M(CO)_2(L)COCH_3 \rightarrow h^5\text{-}C_5H_5M(CO)_2(L)CH_3 + CO \qquad (2)$$

(M = Mo, W)

Whereas these reactions occur at 60° in acetonitrile (M = Mo) with half-lives of the order of 10 - 20 hours [10], only traces of the phosphine-substituted tungsten methyls are observed after several days in refluxing acetonitrile. We were unable to investigate the decarbonylation reactions of the chromium acetyls as they decompose rapidly in solution at temperatures above 25°.

The steric course of the general reaction 1 is independent of both the Group VI metal and the phosphine, with *trans* acetyl complexes being the sole isolable product in all the cases studied to date. In principle these complexes could exist as either *cis* or *trans* isomers (Fig. 1.), but the exclusive formation of the *trans* isomers is shown clearly by NMR spectroscopy. All of the complexes exhibit doublet C_5H_5 proton resonances due to ^{31}P coupling with the ring protons (*J*(PH) 1.5 - 2.0 Hz). The C_5H_5 protons of *cis* isomers of complexes having the general formula h^5-$C_5H_5M(CO)_2(L)X$ (L = PR_3; X = H, alkyl, a halogen, etc.) exhibit singlet resonances (*J*(PH) $\leqslant$ 3 Hz) [1,16 - 18]. There is at present no definitive explanation of this "singlet = *cis*, doublet = *trans*" criterion, although George and Turnipseed [19] have recently suggested that the ^{31}P-ring hydrogen coupling is a through-space interaction, with the phosphorus atom being nearer the ring in the *trans* isomers. While this suggestion seems

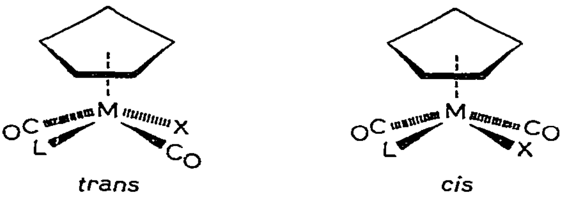

Fig. 1.

TABLE 2

INFRARED SPECTRA AND FORCE CONSTANTS FOR $(h^5\text{-}C_5H_5)M(CO)_2(L)COCH_3$ COMPLEXES[a]

M	L	ν(CO)(cm^{-1})	ν(CO)(acetyl) (cm^{-1})	k (mdyne/Å)	k_i
Cr	$P(C_6H_5)_3$	1932, 1856	1644	14.49	0.58
Cr	$P(p\text{-}CH_3OC_6H_4)_3$	1929, 1850	1642	14.42	0.61
Cr	$P(C_6H_5)(CH_3)_2$	1924, 1841	1643	14.31	0.64
Mo	$P(C_6H_5)_3$	1941, 1853	1598	14.54	0.67
Mo	$P(p\text{-}CH_3OC_6H_4)_3$	1948, 1858	1601	14.65	0.68
Mo	$P(C_6H_5)(CH_3)_2$	1930, 1849	1628	14.42	0.62
Mo	$P(n\text{-}C_4H_9)_3$	1933, 1851	1620	14.46	0.63
W	$P(C_6H_5)_3$	1938, 1853	1605	14.52	0.65
W	$P(p\text{-}CH_3OC_6H_4)_3$	1934, 1848	1598	14.45	0.65
W	$P(C_6H_5)(CH_3)_2$	1928, 1841	1606	14.37	0.66
W	$P(n\text{-}C_4H_9)_3$	1931, 1841	1591	14.38	0.69

[a] Spectra recorded on a Perkin-Elmer 521 Spectrometer in carbon tetrachloride or cyclohexane solutions, 0.1 mm KBr cells.

reasonable, further data on this point are sorely needed*. Definitive assignment of *trans* geometry to the complexes isolated in this study is made possible by applying the criteria of Mawby [17] and Faller [16] to the NMR spectra of the $P(C_6H_5)(CH_3)_2$ derivatives. Both $h^5\text{-}C_5H_5M(CO)_2[P(C_6H_5)(CH_3)_2]COCH_3$ (M = Cr or W) show the expected doublet C_5H_5 resonance and in addition the methyl protons of the ligand appear as a doublet (Table 2). If the complexes were the *cis* isomers, the metal atom would be a site of asymmetry and the magnetically nonequivalent methyl hydrogens would give rise to a pair of doublets [16,17]. We have previously used these criteria in assigning *trans* stereochemistry to the isostructural molybdenum acetyl complexes [10]. In addition, the infrared spectra of the complexes exhibit two terminal CO stretching bands (Table 3), with the lower frequency band being the more intense in all cases. This intensity pattern has been shown by Manning [20] to be indicative

TABLE 3

PROTON NMR DATA FOR $(h^5\text{-}C_5H_5)M(CO)_2(L)COCH_3$ COMPLEXES[a]

M	L	δC_5H_5[b]	δCH_3CO[c]	Ligand Resonances[d]
Cr	$P(C_6H_5)_3$	4.48	2.63	7.3(m), C_6H_5
Cr	$P(p\text{-}CH_3OC_6H_4)_3$	4.58	2.60	7.2(m), C_6H_4; 3.8(s), OCH_3
Cr	$P(C_6H_5)(CH_3)_2$	4.60	2.70	2.0(d, J(PH) = 9.0) CH_3; 7.3(m), C_6H_4
Mo	$P(C_6H_5)_3$	5.03	2.65	7.3(m), C_6H_5
Mo	$P(p\text{-}CH_3OC_6H_4)_3$	5.07	2.60	7.3(m), C_6H_4; 3.85(s), OCH_3
Mo	$P(C_6H_5)(CH_3)_2$	4.98	2.65	2.0(d, J(PH) = 8.5) CH_3; 7.2(m), C_6H_5
Mo	$P(n\text{-}C_4H_9)_3$	5.13	2.53	2.0-0.8 (broad multiplet)
W	$P(C_6H_5)_3$	5.10	2.61	7.4(m), C_6H_5
W	$P(p\text{-}CH_3OC_6H_4)_3$	5.08	2.60	3.85(s), OCH_3; 7.2(m), C_6H_4
W	$P(C_6H_5)(CH_3)_2$	5.05	2.60	2.04(d, J(PH) = 8.5), CH_3; 7.4(m), C_6H_5
W	$P(n\text{-}C_4H_9)_3$	5.20	2.55	2.0-0.7 (broad multiplet)

[a] Varian Associates T-60 Spectrometer, $CDCl_3$ solvent. Chemial shifts vs. internal TMS. [b] All C_5H_5 resonances appear as doublets, J(PH) = 1.5-2.0 Hz. [c] All $COCH_3$ resonances sharp singlets. [d] Coupling constants in Hz. Multiplicity abbreviations: s = singlet, d = doublet, m = multiplet.

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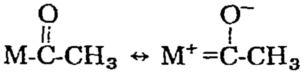
* See Note added in proof, p. 130

of *trans* geometry in this type of comples. While this criterion is thought to be less rigorous as a structure proof than NMR spectroscopy [16,18], taken together with the latter it serves as convincing evidence for the stereochemical assignments made here.

The infrared (Table 2) and proton NMR spectra (Table 3) of the h^5-C_5H_5-$M(CO)_2(L)COCH_3$ complexes provide insight into the electron distribution and bonding in these systems, as a function of both the metal and the phosphorus ligand. The approximate infrared stretching force constants* generally decrease with increasing ligand basicity [23,24], $P(C_6H_5)_3 > P(p\text{-}CH_3OC_6H_4)_3 > P(C_6H_5)(CH_3)_2 \cong P(n\text{-}C_4H_9)_3$, regardless of the central metal**. This is in accord with similar data collected for $LW(CO)_5$ [23,24] and $LNi(CO)_3$ [25] complexes, and is interpreted as being due to increased back-bonding as ligand basicity (and thus electron density at the metal) increases. For a given ligand the force constants decrease in the order Mo > W > Cr indicating increased back bonding in the same order. This is at variance with the usual order found [12,21] for octahedral Group VI metal carbonyls, (W ≫ Cr > Mo) and indicates that the trends noted here should be treated with caution. The low symmetry and increased importance of steric effects (relative to six-coordinate complexes) in the complexes studied here must be borne in mind. Considering the irregular geometry of the subject complexes, relatively minor deviations in metal—ligand bond angles could lead to considerable differences in overlap of metal and ligand orbitals. Such effects would be expected on proceeding from chromium to molybdenum (change in metal atomic radius) [11] or from triphenyl- to tri-n-butyl-phosphine (change in steric demand of the phosphorus ligand) [10].

The infrared spectra of the chromium complexes show an additional feature which suggests that electron density is distributed differently than in the molybdenum and tungsten acetyls. The chromium acetyl CO stretching frequency is considerably higher than expected. This indicates that back-bonding into the acetyl group (shown by the resonance structures below) [6,26,27] is



$$M\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 \leftrightarrow M^+{=}\overset{\overset{\displaystyle O^-}{|}}{C}\text{-}CH_3$$

considerably less important for chromium than for the heavier Group VI elements, and that a greater share of electron density must be distributed to other ligands. This view is in accord with both the force constants calculated for these complexes and with the relatively large upfield shift of the C_5H_5 protons in the chromium derivatives (Table 3).

Only in the case of the tungsten acetyls have we been able to collect useful mass spectral data. The complexes h^5-$C_5H_5W(CO)_2(L)COCH_3$, L = $P(C_6H_5)(CH_3)_2$ or $P(n\text{-}C_4H_9)_3$, exhibit prominent parent ions and fragments corresponding to competing loss of CH_3 and CO groups: $[P{-}CH_3]^+$, $[P{-}CO]^+$, $[P{-}CH_3,CO)^+$ etc. The ions, $[C_5H_5WL]^+$, $[C_5H_5W]^+$ and $[W]^+$ are observed in

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[*] Calculated using the secular equations $\lambda_1 = \mu(k-k_i)$, $\lambda_2 = \mu(k+k_i)$ appropriate to idealized C_s symmetry [21,22].

[**] The complex M = Mo, L = $P(p\text{-}CH_3OC_6H_4)_3$ is an obvious exception. At present we have no explanation for this result.

low abundance. Rational spectra could not be determined for the chromium and molybdenum complexes, apparently due to decomposition at the elevated source temperatures (120 - 150°) required by the involatility of the complexes. This again reflects the relatively great thermal stability of the tungsten complexes.

A reaction characteristic of the molybdenum complexes $h^5\text{-}C_5H_5Mo(CO)_2(L)R$ is the cleavage reaction with iodine to form the iodo complexes $h^5\text{-}C_5H_5Mo(CO)_2(L)I$ [14]. We have extended our investigations to the corresponding reactions of the acetyl complexes described here. Only decomposition was observed with the chromium complexes, a result not unexpected due to previous observations [28] on the extreme instability of $h^5\text{-}C_5H_5Cr(CO)_2[P(OC_6H_5)_3]I$. The reaction of I_2 with $h^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]COCH_3$ yielded the expected iodo complex in 66% yield according to eqn 3. The product

$$h^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]COCH_3 + I_2 \rightarrow h^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]I \quad (3)$$

duct was characterized by elemental analysis, infrared and proton NMR spectroscopy and shown to be a mixture of *cis* and *trans* isomers. Strong terminal CO absorptions are observed at 1960 and 1876 cm^{-1}. The lower frequency band is the more intense, suggesting that the *trans* isomer is the predominant species present in solution [20]. This was confirmed by the NMR spectrum, which exhibited a sharp singlet at δ 5.47 ppm (*cis* isomer) and a doublet at δ 5.15 ppm (J(PH) 2.0 Hz, *trans* isomer) in a 35/65 ratio, respectively. The thermal substitution reaction of $h^5\text{-}C_5H_5W(CO)_3I$ with triphenylphosphine is reported [19] to yield $h^5\text{-}C_5H_5W(CO)_2[P(C_6H_5)_3]I$ as a mixture of isomers but with the *cis* product being the major constituent. At present we are unable to account fully for this difference, but suggest that the different isomer ratios obtained in the thermal substitution reaction [19] and in the present work may be due to the different synthetic routes employed.

In conclusion, we find the chemistry of the related Group VI complexes $h^5\text{-}C_5H_5M(CO)_3CH_3$ and $h^5\text{-}C_5H_5M(CO)_2(L)COCH_3$ to have many features in common. Variations arise from the expected differences in thermal and oxidative stabilities and metal—carbon bond strengths.

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Note added in proof

An alternative explanation of the "singlet = *cis*, doublet = *trans*" phenomenon (p. 126) based on changes in hybridization at phosphorus and of the sign of J (PH) has recently been presented (J.D. Kennedy, W. McFarlane and D.S. Rycroft, Inorg. Chem., 12 (1973) 2742.)