TETRACARBONYL DIKETONE ANIONS OF THE GROUP VI TRANSITION METALS

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SUMMARY

A number of new tetracarbonyl diketonate anions of the Group VI transition metals have been synthesized by two separate routes. The most versatile preparation is by the reaction of a thallium(I) salt of a β-diketone with the metal pentacarbonyl halide anions. The infrared spectra of these anions have been studied in some detail and a number of interesting trends are observed when the Cotton–Kraihanzel force constants are compared. The [Mo(CO)$_4$(Diket)]$^-$ anions will undergo oxidative elimination reactions with allyl chlorides and dimethyltin dichloride and simple substitution reactions with some Lewis bases.

INTRODUCTION

The number of known complexes of the Group VI metal carbonyls with neutral Lewis base ligands, both monodentate and multidentate is enormous (see for example ref. 1). In comparison, relatively few complexes containing negatively charged ligands have been reported. A fair number of compounds of all three Group VIb metals with a variety of uninegative monodentate ligands are known[2,3], the majority of which have halide or pseudohalide substituents. Although there have apparently been no Group VI metal carbonyl complexes containing β-diketonate ligands prepared, a recent communication[4] described the preparation of both pentacarbonyl and tetracarbonyl complexes of these metals with monothiothenoyltrifluoroacetone in which the ligand can function as either a monodentate ligand or a chelating bidentate group.

Carbonyl complexes of Cr, Mo and W containing the B$_3$H$_8^-$ ligand and Mo and W complexes with various chelating polypyrazolylborate ligands have been prepared[5,6], and these seem to be among the few other reported carbonyl complexes of these metals with charged bidentate ligands. Although there have been no Group VI metal carbonyl β-diketonate complexes previously reported, β-diketonate complexes of some other transition metal carbonyls such as Mn(CO)$_4$(Hfacac)[7] and a variety of Rh(CO)$_2$(Diket)[8] and Ir(CO)$_2$(Diket)[9] complexes have been well characterized.

RESULTS AND DISCUSSION

The tetracarbonyldiketonate anions of all the Group VIb metals are very

easily prepared by either of two methods; the first method, although very simple and direct, is not very general and involves the reaction of a quaternary ammonium or similar diketonate salt with the metal carbonyl at temperatures of approximately 130°.

$$R_4N^+Diket^- + M(CO)_6 \xrightarrow[130°]{\text{diglyme}} R_4N^+[M(CO)_4(Diket)]^- + 2CO$$
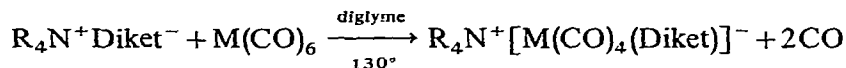
The reaction proceeds smoothly to give good yields but is limited by the availability of the diketonate salts, which, unfortunately, are not always readily available or easily prepared. Alkali metal salts of the β-diketones are fairly easily prepared but do not appear to react to give the desired product unless one uses a solvent which will form a stable complex with the alkali metal cation. Thus sodium acetylacetonate will react with $Mo(CO)_6$ in diglyme as follows:

$$Na(C_5H_7O_2) + Mo(CO)_6 \xrightarrow[130°]{\text{diglyme}} Na(diglyme)_2[Mo(CO)_4(C_5H_7O_2)] + 2CO$$
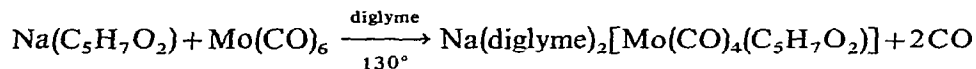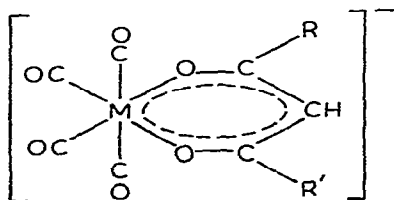
No identifiable products are obtained if one uses non-complexing solvents such as chlorobenzene or similar materials. The alternate method of preparation involves the reaction of a thallium(I) salt of a β-diketone with a metal pentacarbonyl halide salt according to the following equation.

$$Tl(Diket) + A^+[M(CO)_5X]^- \xrightarrow[\text{reflux}]{\text{THF}} A^+[M(CO)_4(Diket)]^- + TlX + CO$$
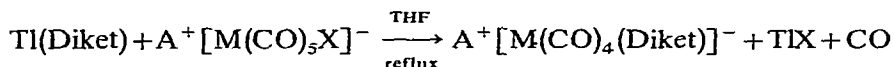
Both starting materials are very easily prepared, thus making this method one of general applicability. An added advantage of this method is the fact that any number of different cations may be used.

The complexes are indefinitely stable under dry nitrogen but decompose slowly in air, the rate depending on the diketonate group and to some extent on the cation. The colors range from pale yellow to red-brown, again depending on the substituents on the β-diketonate ligand. These diamagnetic salts are quite soluble in polar solvents but are, in general, insoluble in hydrocarbons unless the diketonate groups or the cations contain long hydrocarbon chains.

There can be little doubt that these complexes possess an octahedral structure with the β-diketonate ligand coordinating through the oxygen atoms, hence occupying cis positions in the coordination sphere. This type of coordination of the diketonate groups is verified by NMR and more particularly by infrared spectroscopy. The ab-
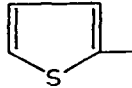

sence of vibrations in the infrared spectra due to free carbonyl groups on the diketone rules out the possibility of coordination via the central carbon atom or of olefin complexes which could be formed by the C=C bond of the enol form of the β-diketone.

The β-diketonate ligands are thus behaving as 3-electron donors and the $[M(CO)_4-(Diket)]^-$ anions satisfy the rare gas configuration rule. The same type of complex with essentially the same structure is formed with ligands which are closely related to the β-diketones such as methyl acetoacetate, tropolone and monothiodibenzoylmethane. In no case was there observed any formation of pentacarbonyl complexes where the diketonate group behaves as a unidentate ligand such as those reported for the monothiothenoyltrifluoroacetone complexes[4], although no attempt was made to

TABLE 1

NMR DATA FOR $[M(CO)_4(DIKET)]^-$ ANIONS

Anion	Ligand	Chemical shifts, τ (ppm)			Mult.	Rel. int.	Assignment
		Cr	Mo	W			
$[M(CO)_4(Acac)]$	$CH_3COCHCOCH_3$	4.93	4.76	4.69	S	1	$=CH-$
		8.32	8.20	8.19	S	6	CH_3
$[M(CO)_4(Bzac)]^-$	$C_6H_5COCHCOCH_3$	≈ 2.4	≈ 2.25	≈ 2.2	M	2	C_6H_5
			≈ 2.6	≈ 2.6	M	3	C_6H_5
		4.20	4.04	3.94	S	1	$=CH-$
		8.14	8.04	8.03	S	3	CH_3
$[M(CO)_4(Dbzm)]^-$	$C_6H_5COCHCOC_6H_5$	≈ 2.2	≈ 2.1	≈ 2.1	M	4	C_6H_5
		≈ 2.6	≈ 2.5	≈ 2.6	M	6	C_6H_5
		3.48	3.33	3.28	S	1	$=CH-$
$[M(CO)_4(Mtdbzm)]^-$	$C_6H_5CSCHCOC_6H_5$		≈ 2.2	≈ 2.15	M	11	C_6H_5 and
			≈ 2.6	≈ 2.55	M		$=CH-$
$[M(CO)_4(Dpm)]^-$	$(CH_3)_3CCOCHCOC(CH_3)_3$	4.36	4.46	4.32	S	1	$=CH-$
		8.99	8.96	8.88	S	18	CH_3
$[M(CO)_4(3\text{-}Me\text{-}Acac)]^-$	$CH_3COC(CH_3)COCH_3$		8.12	8.11	S	6	$CO-CH_3$
			8.21	8.21	S	3	$=C(CH_3)-$
$[M(CO)_4(Ttfac)]^-$	$(C_4H_3S)COCHCOCF_3$		≈ 2.6	≈ 2.6	M	3	
			3.74	3.63	S	1	$=CH-$
$[M(CO)_4(Meacet)]^-$	$CH_3COCHCOOCH_3$			5.28	S	1	$=CH-$
				6.47	S	3	$-CO-OCH_3$
				8.21	S	3	$COCH_3$
$[M(CO)_4(Hfacac)]^-$	$CF_3COCHCOCF_3$	4.61		4.60	S	1	$=CH-$
$[M(CO)_4(Mhpd)]^-$	$CH_3COCHCOCH_2CH(CH_3)_2$		4.78		S	1	$=CH-$
			≈ 8.1		M	3	CH_2 and CH
			8.20		S	3	$COCH_3$
			≈ 9.1		M	6	$(CH_3)_2C$
$[M(CO)_4(3\text{-}Ph\text{-}Acac)]^-$	$CH_3COC(C_6H_5)COCH_3$			2.73	M	5	C_6H_5
				0.42	S	6	CH_3
$[M(CO)_4(Tfacac)]$	$CF_3COCHCOCH_3$	4.49	4.36	4.32	S	1	$=CH-$
		8.10	8.01	8.00	S	3	CH_3

run the reaction under milder conditions that would favor the formation of such complexes.

The NMR spectra of the $A^+[M(CO)_4(Diket)]^-$ complexes are quite simple and easily interpreted. A compilation of NMR data for a number of complexes is given in Table 1. The γ proton resonance of the acetylacetonate group on the $[Mo(CO)_4-(Acac)]^-$ anion occurs at τ 4.76 ppm which is close to the average value of 4.66 ppm determined by Smith and Thwaites[10] for several acetylacetonate complexes. It is perhaps somewhat surprising that the τ value for this resonance is not considerably higher than 4.76 ppm in this anionic complex. In cationic complexes such as $B(Acac)_2^+$ (ref. 11), $(\pi\text{-}C_5H_5)_2Ti(Acac)^+$ (ref. 12) and $Si(Acac)_3^+$ (ref. 13), the γ resonance occurs at very low τ values (3.24, 3.67 ppm and 3.74 ppm respectively) which has been attributed to the net positive charge on the complex[12,14], suggesting that in anionic complexes a shift to higher τ values might occur. No other anionic acetylacetonate complexes appear to have been studied, however, and such a postulate cannot be verified. A comparison of the spectra of $[Cr(CO)_4(Hfacac)]^-$ and $Mn(CO)_4(Hfacac)$ does show the expected trend. The single proton in the Mn derivatives gives a reson-

TABLE 2

FREQUENCIES AND CALCULATED CK FORCE CONSTANTS FOR SOME $[M(CO)_4(Diket)]^-$ ANIONS

Anion	$A_1(1)$	$A_1(2)$	B_1	B_2	k_1	k_2	k_i
[W(CO)₄(Acac)]	2001	1818	1869	1754	12.92	15.10	0.50
[W(CO)₄(Tfacac)]	2000	1839	1880	1789	13.36	15.15	0.44
[W(CO)₄(Hfacac)]	2000	1849	1880	1796	13.47	15.15	0.44
[W(CO)₄(Bzac)]	1995	1828	1861	1765	13.08	14.99	0.50
[W(CO)₄(Dbzm)]	1988	1823	1849	1776	13.21	14.75	0.47
[W(CO)₄(Mtdbzm)]	1991	1849	1880	1782	13.30	15.24	0.48
[W(CO)₄(3-Ph-Acac)]	1991	1802	1852	1750	12.87	14.85	0.50
[W(CO)₄(Dpm)]	1988	1810	1855	1748	12.83	14.88	0.49
[W(CO)₄(Ttfac)]	2002	1827	1863	1765	13.09	15.04	0.51
[W(CO)₄(Trop)]	1989	1841	1885	1778	13.20	15.21	0.43
[W(CO)₄(Meacet)]	1998	1842	1905	1765	13.01	15.51	0.43
[W(CO)₄(3-Me-Acac)]	1989	1824	1842	1774	13.21	14.70	0.50
[Mo(CO)₄(Acac)]	2000	1839	1865	1779	13.28	15.05	0.50
[Mo(CO)₄(Tfacac)]	2002	1829	1890	1754	12.83	15.35	0.46
[Mo(CO)₄(Hfacac)]	2007	1851	1888	1801	13.54	15.27	0.44
[Mo(CO)₄(Bzac)]	2000	1839	1874	1776	13.22	15.14	0.48
[Mo(CO)₄(Dbzm)]	1995	1833	1858	1779	13.27	14.92	0.49
[Mo(CO)₄(Mtdbzm)]	2002	1849	1900	1789	13.34	15.42	0.42
[Mo(CO)₄(Mhpd)]	2015	1818	1888	1750	12.87	15.39	0.50
[Mo(CO)₄(Dpm)]	2010	1811	1886	1749	12.82	15.30	0.47
[Mo(CO)₄(Ttfac)]	2007	1839	1883	1778	13.25	15.26	0.47
[Mo(CO)₄(3-Me-Acac)]	1995	1824	1866	1775	13.17	14.96	0.45
[Cr(CO)₄(Dpm)]	1983	1830	1848	1792	13.41	14.67	0.44
[Cr(CO)₄(Acac)]	2005	1848	1877	1795	1348	15.17	0.47
[Cr(CO)₄(Tfacac)]	2004	1857	1890	1799	13.51	15.30	0.44
[Cr(CO)₄(Hfacac)]	2009	1862	1898	1821	13.78	15.33	0.39
[Cr(CO)₄(Bzac)]	1998	1855	1880	1790	13.41	15.21	0.47
[Cr(CO)₄(Dbzm)]	2000	1851	1901	1790	13.35	15.41	0.41

ance signal at τ 3.85[7] ppm while the anionic Cr complex gives a signal considerably upfield at τ 4.61 ppm.

As one goes from the chromium to the molybdenum to the tungsten complexes, there is observed in all cases a shift in the resonances of the β-diketonate protons to lower fields. The effect is largest for the γ proton (τ 4.93; 4.76 and 4.69 ppm for the acetylacetonate complexes of Cr, Mo and W respectively), however, a definite trend in the same direction, although of smaller magnitude, exists for the other resonances also. Presumably, this shift is due to the lesser amount of shielding of the protons arising from the lower electron density on the diketonate groups as one goes down the periodic table.

The infrared spectra of all the $M(CO)_4(Diket)^-$ complexes in the carbonyl stretching region are qualitatively very typical of spectra for cis-$M(CO)_4X_2$ complexes[15], consisting of four bands as predicted by group theory. The frequencies of the $C\equiv O$ stretching vibrations for a number of $M(CO)_4(Diket)^-$ anions is given in Table 2. The frequencies of the carbonyl stretching bands in these complexes are in general a good deal lower than those in typical neutral complexes of the Group VI metals containing a variety of different ligands[16] as is expected. The only other type of anionic tetracarbonyl complexes of the Group VI metals containing chelating groups are the $[M(CO)_4B_3H_8]^-$ anions and the $C=O$ stretching vibrations occur at low frequencies for these anions also {2028, 1908, 1881 and 1850 cm^{-1} for the $[Mo(CO)_4(B_3H_8)]^-$ anion} but not as low as for the $[M(CO)_4(Diket)]^-$ anions {2000, 1865, 1839, and 1779 for the $[Mo(CO)_4(Acac)^-]$ anion}.

Force constants for the carbonyl stretching vibrations were calculated by the approximate method of Cotton and Kraihanzel[17] (CK) for a large number of $[M(CO)_4-(Diket)]^-$ anions and similar anions (see Table 2 for the calculated force constants) in order to obtain a measure of the relative electron donor and acceptor properties of the metals and ligands. Slight deviations from C_{2v} symmetry due to the asymmetry of some of the diketonate groups were neglected. The symmetry species of the four infrared active vibrations are $2A_1$, B_1 and B_2, but the assignment is dependent on the type of ligand present in the complex. In studying a variety of different complexes of this type, Cotton and Kraihanzel[17,18] assigned the highest frequency band as being of A_1 species and the lowest frequency band of B_2 species in all cases. Of the two bands of intermediate frequency, the highest of these is usually of B_1 species if the donor atom of the ligand is P or S, but is of A_1 species for nitrogen donor ligands. The latter assignment also holds true for the diketonate ligands. These four normal modes can be illustrated as follows:


A_1 (1) B_1 A_1 (2) B_2
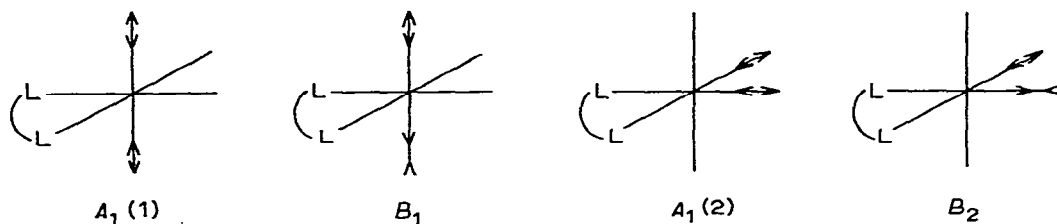
In the simplified CK calculations three force constants are determined; k_1, corresponding to the stretching of the CO groups $trans$ to the substituent ligands; k_2,

the force constant for the stretching of the *cis* CO groups; and an interaction constant k_i. Examination of the force constant data determined for the $[M(CO)_4(Diket)]^-$ anions reveals some interesting, although predictable, trends. As expected, the force constants k_1 and k_2 calculated for the $[M(CO)_4(Diket)]^-$ anions are in general much smaller than those calculated for neutral complexes while the interaction constant k_i is larger. {Compare k_1, k_2 and k_i for $[Mo(CO)_4(Acac)]^-$ of 13.32, 15.08 and 0.50 mdynes/Å with 13.92;15.53 and 0.41 for Mo(Bipy)(CO)$_4$(from Bonati and Wilkinson's data[8]) and 13.76, 15.25 and 0.42 for Mo(En)(CO)$_4$}[18]. An even more striking comparison can be made between $[Cr(CO)_4(Hfacac)]^-$ and the isoelectronic compound $Mn(CO)_4(Hfacac)$; k_1, k_2 and k_i are 13.78, 15.33 and 0.39 for the Cr complex and 15.61, 17.55 and 0.25 for the Mn compound (calcd. from the frequencies in ref. 8). The lowering of k_1 and k_2 for the $[M(CO)_4(Diket)]^-$ anions when compared to either similar neutral complexes with the same central metal or to isoelectronic complexes of the Group VII metals can be attributed mainly to the overall negative charge on the ionic species. This, of course, results in a greater amount of metal carbonyl π bonding (back-bonding), hence, a decrease in the CO stretching force constants. The comparison between $[Cr(CO)_4(Hfacac)]^-$ and $Mn(CO)_4(Hfacac)$ is perhaps the most meaningful one since all the ligands are identical and there are no complicating effects such as differences in the π acceptor ability and inductive effects of the chelating group.

If one examines the CO stretching force constants for a number of $[M(CO)_4(Diket)]^-$ anions where the metal remains the same but the substituents on the diketonate group are varied, then these force constants appear to provide a means of measuring the relative electron donor–acceptor properties of the various diketonate ligands. Electron withdrawing groups, either by induction or resonance, should increase the values of k_1 and to a lesser extent k_2; electron donating groups should decrease the value of both. This type of relationship appears to hold quite well for a large number of $[W(CO)_4(Diket)]^-$ complexes not containing substituents on the γ carbon. (The same type of relationship also appears to hold true for the Mo and Cr complexes, however, a number of exceptions can be noted.) Thus, compared to k_1 for $[W(CO)_4(Acac)]^-$ those diketonate complexes with electron donating groups such as the Dpm complexes have lower values of k_1 while the addition of one or two electron withdrawing groups, such as CF_3 or phenyl, shows a successive increase in k_1 as expected.

A final interesting point is the uniform decrease that is observed in k_1 on going from the Cr to the Mo to the W complexes. This type of behavior would be expected purely on the basis of the greater amount of back-bonding expected as one goes from the $3d$ to $5d$ orbitals, however, no regular pattern such as this can be observed for most other *cis*-tetracarbonyl derivatives of the Group VI metals[16].

The $[M(CO)_4(Diket)]^-$ anions are very reactive and appear to undergo reactions typical of many substituted metal carbonyl complexes such as further substitution of the CO groups and "oxidative elimination" reactions; however, few of these reactions have been investigated in any detail. Reaction of $[W(CO)_4(Acac)]^-$ or $[Mo(CO)_4(Acac)]^-$ with simple phosphines such as triphenylphosphine or tri-n-butylphosphine at ambient temperatures or slightly above leads to replacement of one CO group to form complex anions of the type $[M(CO)_3(PR_3)(Acac)]^-$. Phosphites and pyridine also react in a similar manner. Although it is not possible to say with any certainty what the structure(s) of these substituted derivatives are, the IR spectra appear to be quite reminiscent of a "*fac*" configuration, as shown:
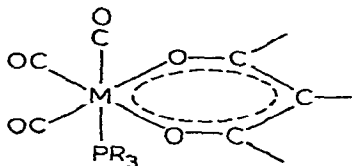
since the CO stretching region consists of a sharp, relatively high frequency band and either a broad band of considerably greater intensity or two closely spaced bands of nearly the same intensity of the first. Although the $[M(CO)_4(Diket)]^-$ anions appeared to react with neutral bidentate ligands such as diphos or bipyridine no well-characterized products were obtained. It is interesting to note that reacting phosphine substituted carbonyl halide salts, such as $(C_2H_5)_4N\{W(CO)_4[P(C_6H_5)_3]Cl\}$ with Tl(Acac) yields only the tetracarbonyl diketonate derivatives, no $[M(CO)_3(PR_3)-(Acac)]^-$ salts being formed.

The ability of certain substituted Group VI metal carbonyl complexes such as $Mo(CO)_4(Bipy)$ to undergo "oxidative elimination" reactions with allyl chloride or certain alkyltin halides is well known[19]. Such reactions will also occur with the $[M-(CO)_4(Diket)]^-$ anions and in general these anionic species react a good deal faster than most neutral complexes such as $Mo(CO)_4(Bipy)$. Thus, allyl chloride reacts with $[Mo(CO)_4(Acac)]^-$ at room temperature according to the following equation:

$$[Mo(CO)_4(Acac)]^- + C_3H_5Cl \rightarrow [Mo(\pi\text{-Allyl})(CO)_2(Acac)Cl]^- + 2\,CO$$

These reactions and the resulting complexes will be discussed in greater detail in a later communication.

$[W(CO)_4(Acac)]^-$ reacts with dimethyltin dichloride also at room temperature in THF as follows:

$$[W(CO)_4(Acac)]^- + (CH_3)_2SnCl_2 \rightarrow \{W(CO)_3[(CH_3)_2SnCl](Acac)Cl\}^- + CO$$
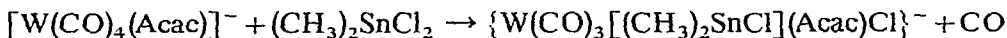
The NMR spectra of this complex anion shows three resonances at τ values of 4.47 (γ-H, Acac); 8.05 (CH_3, Acac) and 9.04 (Sn-CH_3). Only two CO stretching bands are observed in the infrared at 1949 cm^{-1} (s) and 1842 cm^{-1} (vs, b). Presumably this anion has a structure similar to that determined for $Mo(CO)_3(CH_3SnCl_2)(Bipy)Cl$[20] where the coordination about the central metal atom was described as a "capped octahedron." Although the $[M(CO)_4(Diket)]^-$ anions appear to react with a number of compounds very similar to $(CH_3)_2SnCl_2$ such as $(CH_3)_2GeCl_2$, $(CH_3)_2SiCl_2$, $(CH_3)_3SnCl$, CH_3SnCl_3, etc., no other well-defined compounds could be isolated. In most cases it appears that instead of the expected oxidative elimination reactions in which CO is replaced, attack of the $[M(CO)_4(Diket)]^-$ anions by such reagents causes replacement of the diketone ligand. When $HgCl_2$ is treated with an excess of $Et_4N[W(CO)_4(Acac)]$ under very mild conditions the compound $Et_4N^+[W(CO)_3-(Acac)(HgCl)_2]^-$ is formed which is analogous to $(Bipy)W(CO)_3(HgCl)_2$[21]. This complex appears to be quite stable and is sufficiently soluble in polar organic solvents such as CH_3CN to obtain an NMR spectrum which shows the expected resonances for the anion, consisting of two sharp signals at τ values of 6.52 and 8.04 ppm for the CH and CH_3 groups of the acetylacetonate ligands. The IR spectrum shows three bands in the CO starting region at 1930 (m), 1890 (s) and 1792 cm^{-1} (vs). If one increases the amount of $HgCl_2$ used such that the W/Hg cation is 1/1 or greater, then replacement of

the acetylacetonate group is observed and no compounds which could be characterized were obtained. Similar behavior was noted when $Et_4N[W(CO)_4(Acac)]$ was treated with CH_3I. A compound, whose elemental composition agrees with the formula $(C_2H_5)_4N[W(CO)_4(CH_3)I]$, is obtained by elimination of the acetylacetonate ligand. The infrared spectrum of the compound (bands observed at 2066 (w), 1898 (vs, bd) and 1859 cm^{-1} (s) is also consistent with the above formula if one assumes that two of the expected four bands are unresolved, as is often the case with cis-tetracarbonyl complexes[15].

EXPERIMENTAL

General

    Analyses. Elemental analyses were carried out by the Analytical and Information Division, Esso Research and Engineering Co., and by Clark Microanalytical

TABLE 3

ANALYTICAL DATA FOR $[M(CO)_4(Diket)]^-$ AND RELATED SALTS

Compound	Found (%)			Calculated (%)		
	C	H	N (P)	C	H	N (P)
$(C_2H_5)_4N[W(CO)_4(Acac)]$	39.11	5.44	2.61	38.87	5.09	2.67
$(C_6H_5)_4P[W(CO)_4(Tfacac)]$	49.75	3.30	4.16	50.25	3.07	3.93
$(C_6H_5)_4As[W(CO)_4(Hfacac)]$	44.92	2.96	8.20^a	44.72	2.38	8.45^a
$(C_2H_5)_4N[W(CO)_4(Bzac)]$	44.85	6.04	2.51	44.99	6.45	2.39
$(C_2H_5)_4N[W(CO)_4(Dbzm)]$	50.12	4.96	2.20	49.93	4.83	2.16
$(C_2H_5)_4N[W(CO)_4(Dpm)]$	45.21	6.75	2.11	45.33	6.45	2.30
$(C_2H_5)_4N[W(CO)_4(Mtdbzm)]$	48.37	4.94	1.97	48.73	4.72	2.11
$(C_2H_5)_4N[W(CO)_4(3-Ph-Acac)]$	45.66	5.94	2.85	45.94	5.20	2.33
$(C_2H_5)_4N[W(CO)_4(Ttfa)]$	37.71	4.30	2.47	37.05	3.76	2.17
$(C_2H_5)_4N[W(CO)_4(trop)]$	41.30	5.04	2.51	41.70	4.63	2.57
$(C_2H_5)_4N[W(CO)_4(Meacet)]$	37.57	4.97	2·79	37.72	5.00	2.59
$(C_6H_5)_4P[W(CO)_4(3-Me-Acac)]$	54.70	4.00	4.18	54.55	3.91	4.14
$(C_2H_5)_4N[Mo(CO)_4(Acac)]$	46.23	5.86	3.51	46.69	6.23	3.21
$(C_2H_5)_4N[Mo(CO)_4(Tfacac)]$	40.72	4.66	3.04	41.55	4.92	2.85
$(n-C_4H_9)_4N[Mo(CO)_4(Hfacac)]$	45.95	6.13	2.25	45.70	5.57	2.13
$(C_2H_5)_4N[Mo(CO)_4(Bzac)]$	52.98	6.18	2.93	52.91	5.86	2.81
$(C_2H_5)_4N[Mo(CO)_4(Dbzm)]$	57.02	6.07	2.68	57.76	5.57	2.68
$(n-C_4H_9)_4N[Mo(CO)_4(Mtdbzm)]$	60.94	6.77	2.36	60.90	6.86	2.03
$(C_2H_5)_4N[Mo(CO)_4(Mhpd)]$	49.46	7.40	3.32	50.32	6.93	2.93
$(C_2H_5)_4N[Mo(CO)_4(Dpm)]$	52.64	7.88	2.51	52.97	7.54	2.69
$(C_2H_5)_4N[Mo(CO)_4(Ttfac)]$	43.50	4.66	2.37	42.94	4.32	2.50
$(C_6H_5)_4N[Mo(CO)_4(3-Me-Acac)]$	61.19	4.73	4.65	61.82	4.42	4.69
$(C_6H_5)_4P[Cr(CO)_4(Dpm)]$	68.13	5.72	5.08	68.21	5.72	4.51
$(C_6H_5)_4P[Cr(CO)_4(Acac)]$	65.18	4.39	5.14	65.75	4.52	5.14
$(C_6H_5)_4P[Cr(CO)_4(Tfacac)]$	59.75	3.92	4.92	60.38	3.68	4.72
$(C_6H_5)_4P[Cr(CO)_4(Hfacac)]$	54.95	3.34	4.68	55.41	2.96	4.33
$(C_6H_5)_4As[Cr(CO)_4(Bzac)]$	64.37	4.21	10.17^a	64.40	4.12	10.58^a
$(C_2H_5)_4N[Cr(CO)_4(Dbzm)]$	61.91	5.87	2.73	62.66	6.04	2.70

^{a} Percent As.

TABLE 4

ANALYTICAL DATA AND INFRARED FREQUENCIES IN THE CO STRETCHING REGION FOR SOME DERIVATIVES OF THE $[M(CO)_4(Diket)]^-$ IONS

Compound	Found (calcd.) (%)				$v(CO)$ (cm^{-1})	
	C	H	N(P)	Cl		
$(C_2H_5)_4N\{W(CO)_3(Acac)[P(C_6H_5)_3]\}$	53.17 (53.76)	5.35 (5.58)	1.66 (1.85)		1869, 1721	1751
$(C_2H_5)_4N\{W(CO)_3(Acac)[P(n-C_4H_9)_3]\}$	47.55 (48.07)	7.67 (7.78)	1.94 (2.00)		1866, 1712	1748
$(C_2H_5)_4N\{W(CO)_3(Acac)[(CH_3)_2SnCl]Cl\}$	29.70 (30.03)	4.40 (4.64)	2.10 (1.95)	10.48 (9.89)	1949	1842
$(C_2H_5)_4N[Mo(CO)_3(Acac)(C_5H_5N)]$	51.43 (51.64)	6.89 (6.60)	5.21 (5.73)		1864	1719
$(C_2H_5)_4N\{Mo(CO)_3(Acac)[P(OC_2H_5)_3]\}$	46.28 (45.91)	7.60 (7.35)	2.76 (2.43)		1899, 1730	1812
$(C_2H_5)_4N[W(CO)_3(Acac)(HgCl)_2]$	20.38 (19.83)	3.00 (2.81)	2.18 (1.45)	7.65 (7.32)	1930, 1792	1890
$(C_2H_5)_4N[W(CO)_4(CH_3)I]$	26.67 (27.49)	3.46 (4.08)	2.33 (2.46)	22.75[a] (22.31)[a]	2066, 1859	1898

[a] Percent I

Laboratory, Urbana, Illinois. The results for a number of $[M(CO)_4(Diket)]^-$ and related salts are given in Table 3 and the results for several derivatives of these salts are given in Table 4.

Spectra. Infrared spectra were obtained either on a Perkin–Elmer Model 521 Infrared Spectrometer or on a Beckman Model 20 Infrared Spectrometer. Spectra were obtained either as solutions in CH_2Cl_2 or as Nujol mulls between KBr plates. NMR spectra were obtained on a Varian Model A-60 NMR spectrometer usually as solutions in CD_3CN.

Preparation of $[M(CO)_4(Diket)]^-$ and related salts

Because of the sensitivity of many of the products to oxygen and moisture, all work was carried out in a dry-box under a nitrogen atmosphere and carefully dried solvents were used throughout.

Reagents. The preparation of 3-phenyl-2,4-pentanedione and 3-methyl-2,4-pentanedione were carried out as described by Hauser and Adams[22] and Taylor and McKillop[23] respectively. Monothiodibenzoylmethane was prepared by the method of Uhlemann and Müller[24]. All other ligands were obtained from commercial sources. The metal pentacarbonyl halide salts were synthesized by the method of Abel, Butler and Reid[25] and tetrabutylammonium acetylacetonate was obtained by the procedure described by Brandström and Junggren[26].

Method A. To an Erlenmeyer flask containing 30–40 ml THF and a magnetic stirring bar is added 0.02 mole of the metal pentacarbonyl halide salt (the cation or halide are unimportant). To this mixture is added an exactly equivalent amount of the thallium diketonate salt (prepared by reacting $TlOC_2H_5$ with a slight excess of the β-diketone in a hydrocarbon solvent) and the resulting mixture is heated to the boiling point with stirring. After the reaction is complete (approximately 5 min) the hot solution is filtered through a fine fritted glass funnel. The filtrate is added to 150 ml pentane

precipitating the tetracarbonyl diketonate salt. The pentane is decanted off and the salt washed with additional pentane and is then collected on a filter. Pure samples can be obtained by recrystallization from THF. (Occasionally the salts will separate as oils, but these will usually crystallize after scratching the flask with a glass rod.) The yields obtained are nearly quantitative. See Table 1 for analytical data.

Method B. To an Erlenmeyer flask, containing 50 ml diglyme, 0.0205 mole of the metal hexacarbonyl and a magnetic stirring bar, is added 0.020 mole of the alkali metal or tetraalkylammonium salt of the β-diketone [such as $(n\text{-}C_4H_9)_4N^+C_5H_7\text{-}O_2^-$]. The mixture is heated to $125°$ with stirring and maintained at that temperature until CO evolution ceases (usually less than 20 min). The hot solution is filtered and after the yellow filtrate has cooled, 200 ml of pentane is added. The yellow solid, which precipitates, is separated from the solvent by decantation and is washed several times with additional fresh pentane. The solid is collected on a filter and washed with additional pentane and dried. Trace amounts of the unreacted metal carbonyl can be sublimed out by gently warming under vacuum.

Reaction of $[M(CO)_4(Acac)]^-$ *salts*

A. Reaction with unidentate Lewis bases. A twofold molar excess of the Lewis Base [pyridine, $P(OC_2H_5)_3$, $P(C_6H_5)_3$ or $P(n\text{-}C_4H_9)_3$] is slowly added to a solution or suspension of 1–2 g of the $[M(CO)_4(Acac)]^-$ salt in 30 ml THF. After the evolution of CO ceases, the mixture is allowed to stand for about 1 h with stirring then filtered. The filtrate is added to 100 ml pentane precipitating the $[M(CO)_3L(Acac)]^-$ salt. This is collected on a filter, washed with pentane, and dried.

B. Reaction of $(C_2H_5)_4N[W(CO)_4(Acac)]$ *with* $HgCl_2$. A solution of 1.36 g (0.005 mole) $HgCl_2$ in THF was slowly added to a solution of 5.25 g (0.01 mole) $(C_2H_5)_4\text{-}N[W(CO)_4(Acac)]$ in THF with stirring. Stirring was continued at room temperature for 24 h during which time a yellow solid formed. This was filtered off, washed with a little THF and dried giving 2.3 g of a compound which analyzed for $(C_2H_5)_4\text{-}N[W(CO)_3(Acac)(HgCl)_2]$.

C. Reaction of $(C_2H_5)_4N[W(CO)_4(Acac)]$ *with* $(CH_3)_2SnCl_2$. A concentrated solution of $(CH_3)_2SnCl_2$ in THF was added drop-wise to a solution of 1.35 g (0.0025 mole) $(C_2H_5)_4N[W(CO)_4(Acac)]$ in 35 ml THF at $25°$ with stirring. The solution of $(CH_3)_2SnCl_2$ was added until CO was no longer given off. The solution was filtered and 100 ml pentane was added to the filtrate. The pale yellow solid which formed was collected on a filter, washed with additional pentane and dried. Yield was 1.5 g.

D. Reaction of $[(C_2H_5)_4N(CO)_4(Acac)]^-$ *salts with* CH_3I. A five-fold molar excess of CH_3I was added to a solution containing 0.01 mole of the $[M(CO)_4(Acac)]^-$ salt in 35 ml THF. The mixture was stirred and the color gradually turned deep red-brown. The mixture was allowed to react for 3 h at room temperature and was then filtered. The filtrate was evaporated on a rotary evaporator giving a deep brown solid residue. This was dissolved in THF and the THF solution was added to pentane. A green precipitate formed which was collected on a filter and dried.

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