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Organometallic Chemistry of the Transition Metals. XV. New Olefinic and Acetylenic Derivatives of Tungsten[1]

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Reaction of $(CH_3CN)_3W(CO)_3$ with the appropriate olefinic derivative in boiling hexane gives complexes of the types (triene)-$W(CO)_3$ (triene = cycloheptatriene, 1,3,5-cyclooctatriene, cyclooctatetraene, or 6-dimethylaminofulvene), (diene)$W(CO)_4$ (diene = bicyclo[2.2.1]heptadiene or 1,5-cyclooctadiene), and $(C_6H_8)_2W(CO)_2$ (C_6H_8 = 1,3-cyclohexadiene). Methyl vinyl ketone reacts with $(CH_3CN)_3W(CO)_3$ with complete loss of all carbonyl and acetonitrile ligands to give yellow, air-stable, volatile $(CH_3COCH{=}CH_2)_3W$. Cyclopentadiene and pentamethylcyclopentadiene react with $(CH_3CN)_3W(CO)_3$ to give the hydrides $C_5R_5W(CO)_3H$ (R = H or CH_3, respectively). The aromatic hydrocarbons benzene, toluene, *p*-xylene, and mesitylene react with $(CH_3CN)_3W(CO)_3$ to form the known (arene)$W(CO)_3$ complexes. Hexafluorobutyne-2 reacts with $(CH_3CN)_3W(CO)_3$ to form white, air-stable, volatile $[(CF_3)_2C_2]_3W(NCCH_3)$. By syntheses analogous to those of the known[3] molybdenum analogs, the cycloheptatriene complex $C_7H_8W(CO)_3$ has been converted to green-black $C_7H_7W(CO)_2I$ which reacts with sodium cyclopentadienide to give orange $C_5H_5W(CO)_2C_7H_7$.

Introduction

Many chromium and molybdenum complexes of diolefins and triolefins have been prepared by heating the appropriate metal hexacarbonyl with the appropriate olefinic derivative.[4] In these reactions the double bonds of the olefin displace carbonyl groups from the metal hexacarbonyl.

Since the discovery of $C_8H_8Fe(CO)_3$,[5] many laboratories have tried to make analogous cyclooctatetraene complexes of chromium, molybdenum, and tungsten by displacement of carbonyl groups from the hexacarbonyls with cyclooctatetraene. The only tractable product ever obtained from such reactions was the pale yellow molybdenum tetracarbonyl complex of cyclooctatetraene dimer of formula $C_{16}H_{16}Mo(CO)_4$ prepared by Bennett, Pratt, and Wilkinson.[6] No C_8H_8 derivatives were ever isolated from direct reactions of the metal hexacarbonyls with cyclooctatetraene.

Recently Winstein, Kaesz, Kreiter, and Friedrich[7] prepared a molybdenum carbonyl complex of cyclooctatetraene of the formula $C_8H_8Mo(CO)_3$. Their secret of success was the use of (diglyme)$Mo(CO)_3$[8] rather than molybdenum hexacarbonyl. The cyclooctatetraene was found to displace the diglyme ligand from (diglyme)$Mo(CO)_3$ at relatively mild conditions (hexane solution, 50°). Since $C_8H_8Mo(CO)_3$ is thermally unstable, these mild conditions are necessary in order to prevent destruction of the product in the reaction mixture.

The metal–carbon bonds to carbonyl groups have considerable double-bond character owing to partial $d\pi$–$p\pi$ bonding involving back donation of electron pairs in filled metal d orbitals to empty antibonding π^* orbitals of the carbonyl ligands. Such partial $d\pi$–$p\pi$ bonding cannot occur in the metal–oxygen bonds to diglyme or other ether ligands. This appears to account for the easier displacement of diglyme ligands than of carbonyl ligands by olefins.

Tungsten hexacarbonyl is much less suitable than its molybdenum and chromium analogs for the preparation of olefin complexes owing to its great inertness,[9]

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[1] (a) For part XIV of this series, see R. B. King, M. I. Bruce, J. R. Phillips, and F. G. A. Stone, *Inorg. Chem.*, **5**, 684 (1966); (b) for preliminary communications of some of this work, see R. B. King and A. Fronzaglia, *Chem. Commun.*, 547 (1965); 274 (1966).

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[3] (a) D. J. Bertelli, Ph.D. Thesis, University of Washington, 1961; (b) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

[4] E. O. Fischer and H. Werner, "Metall-π-Komplexe mit di- und oligoolefinischen Liganden," Verlag Chemie, Weinheim/Bergstr., Germany, 1963.

[5] T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959); *J. Am. Chem. Soc.*, **82**, 366 (1960); M. D. Rausch and G. N. Schrauzer, *Chem. Ind.* (London), 957 (1959); A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Japan*, **32**, 880 (1959).

[6] (a) M. A. Bennett and G. Wilkinson, *Chem. Ind.* (London), 1516 (1959); (b) M. A. Bennett, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 2037 (1961).

[7] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965).

[8] R. P. M. Werner and T. H. Coffield, *Chem. Ind.* (London), 936 (1960).

[9] R. B. King, Ph.D. Dissertation, Harvard University, 1960; R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3590 (1961).

which makes such preparations difficult, inefficient, or even impossible. The diglyme derivative (diglyme)-$W(CO)_3$ would be a useful precursor to the preparation of olefin derivatives of tungsten carbonyl, but unfortunately this diglyme complex is still unknown.

A readily available substitution product of tungsten carbonyl is the acetonitrile complex $(CH_3CN)_3W(CO)_3$ obtainable in better than 90% yield by prolonged heating of tungsten hexacarbonyl in acetonitrile solution at the boiling point.[10] Since acetonitrile, like diglyme, is a ligand which has very little pπ–dπ bonding ability,[11] it is reasonable to expect that the acetonitrile ligands might be readily displaced by various olefins providing a route to the many olefin derivatives of tungsten carbonyl predicted to be stable compounds but which cannot be prepared directly from tungsten hexacarbonyl. The possible reactivity of $(CH_3CN)_3$-$W(CO)_3$ toward unsaturated compounds is also suggested by the work of Tate, Augl, Ritchey, Ross, and Grasselli,[12] who found it to react readily with acetylenes to form the stable but unusual complexes $(RC\equiv CR')_3WCO$. A precedent for the synthesis of metal–olefin complexes from metal–nitrile complexes is the synthesis of olefin–palladium halide complexes from the benzonitrile complex $(C_6H_5CN)_2PdCl_2$.[13]

This paper describes the details of an extensive study of the reactions of $(CH_3CN)_3W(CO)_3$ with certain olefins and acetylenes. Numerous compounds of various types have been prepared. Some, such as $(CH_3COCH{=}CH_2)_3W$, represent compound types unknown even in chromium and molybdenum chemistry and have prompted related studies with $(CH_3CN)_3$-$Cr(CO)_3$ and $(CH_3CN)_3Mo(CO)_3$ to be described in a future publication. Others, notably the cycloheptatriene complex $C_7H_8W(CO)_3$, have now become available for the first time in quantities sufficient for use as intermediates in the synthesis of other organotungsten compounds of interest; thus from $C_7H_8W(CO)_3$ we have prepared $C_7H_7W(CO)_2I$ and $C_5H_5W(CO)_2C_7H_7$.

Experimental Section

Microanalyses (Tables I and II) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra (Table III) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the metal carbonyl regions of the infrared spectra of selected compounds were investigated in further detail in cyclohexane solution or a Halocarbon oil mull (for compounds insoluble in cyclohexane) and recorded on a Beckman IR-9 spectrometer. Ultraviolet spectra were taken in cyclohexane or dichloromethane solution and recorded on a Cary Model 14 spectrometer. Proton nmr spectra were taken at ~37° in carbon disulfide solution and recorded on a Varian A-60 spectrometer. The ^{19}F nmr spectrum of $[(CF_3)_2C_2]_3W(NCCH_3)$ was taken in CH_2Cl_2 solution at 56.4 Mc and recorded on a Varian HR-60 spectrometer. Mass spectra were recorded at 70-ev electron energies using an Associated Electrical Industries MS-9 spectrometer. The parent ion position established the exact molecular weight of the key compounds in this paper. Melting and decomposition points were determined in capillaries and are uncorrected.

Reagents.—The ligands cyclohepatriene (Shell), cyclooctatetraene (Badische Anilin- und Soda-Fabrik), 1,5-cyclooctadiene (Cities Service), bicyclo[2.2.1]heptadiene (Shell), 1,3-cyclohexadiene (Columbia), methyl vinyl ketone (Borden Monomer-Polymer), dicyclopentadiene (Enjay), aromatic hydrocarbons (Fisher Scientific), hexafluorobutyne-2 (Peninsular ChemResearch), and N,N,N',N'-tetramethylethylenediamine (Aldrich) were all obtained from the indicated commercial sources. 1,3,5-Cyclooctatriene,[14] 6-dimethylaminofulvene,[15] and pentamethylcyclopentadiene[16] were prepared by reported procedures which have been or will be discussed in greater detail in papers emphasizing their complexes.

Tungsten hexacarbonyl was purchased from Pressure Chemical Co., Pittsburgh, Pa., and converted to $(CH_3CN)_3W(CO)_3$ by boiling several days under reflux with acetonitrile according to the published procedure.[10] If the scale of the $(CH_3CN)_3W$-$(CO)_3$ preparations was limited to 20 g of tungsten hexacarbonyl, the $(CH_3CN)_3W(CO)_3$ could be obtained in 90% yields as a yellow solid which slowly became blue upon exposure to air for several days. Attempts to carry out the preparation of $(CH_3CN)_3W$-$(CO)_3$ on a larger scale resulted in a lower yield. When larger quantities of $(CH_3CN)_3W(CO)_3$ were required, several smaller scale reactions were carried out simultaneously.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admission to evacuated flasks.

General Procedure for Reaction of $(CH_3CN)_3W(CO)_3$ with Olefins.—The procedure given here was suitable for the preparations of $C_7H_8W(CO)_3$, $C_8H_{10}W(CO)_3$, $C_8H_8W(CO)_3$, $C_8H_{12}W$-$(CO)_4$, $C_5H_5W(CO)_3H$, $(C_6H_8)_2W(CO)_2$, and $(CH_3COCH{=}CH_2)_3$-W and will not be repeated in detail for each case.

A mixture of 1.17 g (3 mmoles) of $(CH_3CN)_3W(CO)_3$, excess of the olefin (1 to 2 ml depending on its abundance), and 50 ml of hexane was refluxed at the boiling point with magnetic stirring for at least 16 hr. During the reaction period, the yellow insoluble $(CH_3CN)_3W(CO)_3$ gradually dissolved forming a solution with the characteristic color of the olefin complex. However, some insoluble matter always remained during the entire reaction period.

After the reaction period was over, the reaction mixture was filtered hot and the residue washed with a few milliliters of boiling hexane. The filtrate was cooled several hours in a −78° bath. The crystals of complex which separated were filtered off and purified finally by sublimation under the conditions listed in Table I.

Attempts to scale up the reaction led to lower percentage yields. Thus the preparation of $C_7H_8W(CO)_3$ on a 60-mmole scale gave only a 33% yield, the preparation of $(CH_3COCH{=}CH_2)_3W$ on a 50-mmole scale gave only a 30% yield, and the preparation of $(C_6H_8)_2W(CO)_2$ on a 15-mmole scale gave only a 22% yield.

Preparation of $C_5H_4CHN(CH_3)_2W(CO)_3$.—A mixture of 1.17 g (3 mmoles) of $(CH_3CN)_3W(CO)_3$, 0.36 g (3 mmoles) of 6-dimethylaminofulvene, and 50 ml of hexane was refluxed ~18 hr with stirring. A red precipitate of the product formed. After the reaction period was over, this precipitate was filtered, washed with hexane, and dried.

The crude product was extracted with ~100 ml of acetone in five portions and the filtered, deep red acetone extracts were cooled overnight at −78° to deposit 0.285 g of red crystals. After filtration of these crystals, an additional 0.453 g of product was obtained by addition of benzene and solvent removal at ~30 mm. The total yield of $C_5H_4CHN(CH_3)_2W(CO)_3$ thus was 0.738 g (63%).

Preparation of $C_{10}H_{12}W(CO)_4$.—A mixture of 1.17 g (3 mmoles) of $(CH_3CN)_3W(CO)_3$, 1.0 ml (0.98 g, 7.4 mmoles) of dicyclo-

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[15] R. B. King and M. B. Bisnette, *ibid.*, **3**, 801 (1964).

[16] R. B. King and M. B. Bisnette, to be published. See also L. De Vries, *J. Org. Chem.*, **25**, 1838 (1960).

TABLE I

SOME TUNGSTEN OLEFIN COMPLEXES OBTAINED FROM $(CH_3CN)_3W(CO)_3$

Olefin	Product	Yield,[a] %	Color	Mp, °C	Sublimation conditions	Analyses, %	C	H	O	Other
A. (triene)$W(CO)_3$ Compounds										
Cycloheptatriene	$C_7H_8W(CO)_3$	69	Red	115–121 dec (lit.[7] 110)	80° (0.1 mm)	Calcd	33.3	2.2	13.3	
						Found	33.3	2.3	13.5	
1,3,5-Cyclooctatriene	$C_8H_{10}W(CO)_3$	66	Orange	108–113 dec	80° (0.1 mm)	Calcd	35.3	2.7	12.8	
						Found	35.1	2.7	13.2	
Cyclooctatetraene	$C_8H_8W(CO)_3$	28	Red-brown	115–118 dec	85° (0.1 mm)	Calcd	35.5	2.1	12.9	49.5 (W)
						Found	35.0	2.1	13.1	49.1 (W)
6-Dimethylaminofulvene	$C_5H_4CHN(CH_3)_2W(CO)_3$	63	Red		. . .	Calcd	33.9	2.8	12.3	3.6 (N)
						Found	32.8	3.0	13.1	3.6 (N)
B. (diene)$W(CO)_4$ Compounds										
1,5-Cyclooctadiene	$C_8H_{12}W(CO)_4$	76	Yellow	159–162 dec	80° (0.1 mm)	Calcd	35.6	3.0	15.8	45.5 (W)
						Found	36.8	3.4	15.9	43.5 (W)
Bicycloheptadiene (norbornadiene)	$C_7H_8W(CO)_4$	74	Yellow	90–92	80° (0.1 mm)	Calcd	34.0	2.1	16.5	47.4 (W)
						Found	34.7	2.4	16.7	46.4 (W)
Dicyclopentadiene	$C_{10}H_{12}W(CO)_4$	6	Yellow	116–119 dec	90° (0.1 mm)	Calcd	39.2	2.8	14.9	
						Found	39.5	3.0	14.8	
C. (diene)$_2W(CO)_2$ Compound										
1,3-Cyclohexadiene	$(C_6H_8)_2W(CO)_2$	52	Yellow	153–157 dec	130° (0.2 mm)	Calcd	42.0	4.0	8.0	46.0 (W)
						Found	41.7	4.0	8.7	45.5 (W)
D. (dienyl)$W(CO)_3H$ Compounds										
Cyclopentadiene	$C_5H_5W(CO)_3H$	32	Pale yellow	66–68 (lit.[15] 66–67)	85° (0.1 mm)	Calcd	28.7	1.8	14.4	
						Found	29.3	1.9	14.6	
Pentamethylcyclopentadiene	$C_5(CH_3)_5W(CO)_3H$	3 12[b]	Yellow	108–111 dec	80° (0.1 mm)	Calcd	38.6	4.0	11.9	
						Found	39.4	4.3	12.6	
E. (enone)$_3W$ Compound										
Methyl vinyl ketone	$(CH_3COCH{=}CH_2)_3W$	60	Yellow	137–140°	90° (0.1 mm)	Calcd	36.6	4.6	12.2	46.7 (W)
						Found	36.7	4.6	12.2	46.6 (W)

[a] The yields are based on the number of available carbonyl groups in the $(CH_3CN)_3W(CO)_3$ used for the reaction. [b] This yield was obtained when the reaction was carried out in boiling methylcyclohexane solution.

TABLE II

SOME TUNGSTEN ARENE COMPLEXES OBTAINED FROM $(CH_3CN)_3W(CO)_3$

Arene	Product	Yield, %	Color	Mp, °C	Sublimation conditions	Analyses, %	C	H	O
Benzene	$C_6H_6W(CO)_3$	14	Yellow	dec >175	120° (0.2 mm)	Calcd	31.2	1.7	13.9
						Found	31.3	1.7	14.3
Toluene	$CH_3C_6H_5W(CO)_3$	88	Yellow	139–142 dec	120° (0.2 mm)	Calcd	33.3	2.2	13.3
						Found	32.8	2.0	13.4
p-Xylene	$(CH_3)_2C_6H_4W(CO)_3$	9	Yellow	151–154 dec	125° (1 mm)	Calcd	35.3	2.7	12.8
						Found	34.9	2.5	13.1
Mesitylene	$(CH_3)_3C_6H_3W(CO)_3$	65	Yellow	dec >180	140° (1 mm)	Calcd	37.1	3.1	12.4
						Found	36.8	3.0	11.7

pentadiene, and 50 ml of hexane was refluxed at the boiling point with magnetic stirring. Solvent was removed from the filtered reaction mixture at 25° (30 mm). The residue was dried at 25° (0.1 mm) for 1 hr solidifying to yellow crystals. These crystals were extracted with 50 ml of pentane in four portions. The pentane extracts were filtered and concentrated to ~30 ml. Cooling this solution overnight in a −78° bath precipitated yellow crystals. These were filtered, dried, and sublimed at ~90° (0.1 mm) to give 0.071 g (5.5% yield) of yellow $C_{10}H_{12}W(CO)_4$, mp 116–119° dec.

Preparation of $C_5(CH_3)_5W(CO)_3H$.—A mixture of 1.17 g (3 mmoles) of $(CH_3CN)_3W(CO)_3$, 0.5 ml (0.41 g, 3.0 mmoles) of pentamethylcyclopentadiene, and 50 ml of methylcyclohexane was refluxed 21 hr with magnetic stirring. The reaction mixture was filtered at the boiling point and the residue washed with a few milliliters of boiling hexane. The yellow-brown hexane solution was cooled ~26 hr in a −78° bath. The pale yellow crystals which separated were filtered and dried. They were sublimed at 90° (0.1 mm) to give 0.146 g (12% yield) of pale yellow $C_5(CH_3)_5W(CO)_3H$, mp 108–111° dec.

Preparation of the (arene)$W(CO)_3$ Compounds from $(CH_3CN)_3W(CO)_3$.—A mixture of 1.17 g (3 mmoles) of $(CH_3CN)_3W(CO)_3$ and 25–50 ml of the aromatic hydrocarbon (benzene, toluene, *p*-xylene, or mesitylene) was heated at the boiling point or 130° (oil bath) (whichever is lower). After 23 hr (benzene) or 2–5 hr (other arenes), the reaction mixture was cooled to room temperature. Excess arene was removed at ~25° (0.1 mm) (benzene at ~25° (30 mm)) and the yellow crystalline product isolated from the residue by vacuum sublimation at ~120° (0.2 mm). Overheating of the products during sublimation gave a black deposit, apparently metallic tungsten; varying amounts of such decomposition during sublimation may have accounted for the varying yields (Table II).

Preparation of $[(CF_3)_2C_2]_3W(NCCH_3)$.—A 150-ml stainless steel pressure vessel (high-pressure series of Hoke, Inc., Tenakill, N. J.) was charged with 3.91 g (10 mmoles) of $(CH_3CN)_3W(CO)_3$ and 7.0 ml (liquid) (11 g, 68 mmoles) of hexafluorobutyne-2 was distilled in. This reaction vessel was heated at 100° for 48 hr. After cooling to room temperature, the reaction vessel was opened and the contents rinsed out with three 25-ml portions of dichloromethane. Solvent was removed from these dichloromethane solutions at 25° (30 mm).

A brown, solid residue remained. Product was sublimed out of this residue at 100° (0.2 mm) and collected as fuzzy white crystals on a water-cooled probe. This sublimate was washed with ~75 ml of pentane in four portions and dried. Resublimation at 60–100° (0.2 mm) gave a total of 2.184 g (31% yield) of white $[(CF_3)_2C_2]_3W(NCCH_3)$, mp 114–115°, which was collected in

TABLE III: INFRARED SPECTRA OF NEW COMPOUNDS DESCRIBED IN THIS PAPER (CM^{-1})

Compound	ν_{CO} (metal)[a]	ν_{CH}[b]	Other bands[b]
	A. (triene)$W(CO)_3$ Complexes		
$C_7H_8W(CO)_3$	1998 s, 1931 s, 1904 s	3000 vw, 2860 w, 2800 vw	1512 w, 1497 w, 1450 m, 1427 m, 1389 w, 1345 w, 1300 w, 1221 w, 1194 w, 1165 w, 1103 vw, 995 m, 985 w, 965 vw, 940 vw, 881 w, 840 m, 790 m
$C_8H_{10}W(CO)_3$	1999 vs, 1923 vs, 1910 vs	2890 vw, 2850 ww, 2810 vw	1504 vw, 1473 vw, 1442 w, 1430 w, 1423 w, 1396 vw, 1365 vw, 1342 m, 1308 vw, 1282 vw, 1214 w, 1190 vw, 1163 w, 1060 w, 1051 vw, 1041 w, 975 vw, 951 vw, 909 vw, 866 w, 860 vw, 824 vw, 817 vw, 804 vw, 784 vw, 711 vw
$C_8H_8W(CO)_3$	2006 s, 1944 s, 1913 s	2950 vw	1670 m,[d] 1481 vw, 1470 w, 1439 w, 1380 w, 1335 vw, 1260 vw, 1189 vw, 1161 w, 1154 w, 954 vw, 901 vw, 888 m, 845 vw, 820 vw, 811 m, 774 m, 740 vw, 735 vw, 727 vw
$C_5H_4CHN(CH_3)_2W(CO)_3$	1906 w, 1810 sh, 1787 s,[e] 1619 s[c,e]	3070 vw, 3030 vw	1448 w, 1415 sh, 1408 s, 1400 m, 1362 s, 1334 w, 1278 m, 1166 vw, 1128 m, 1090 vw, 1076 vw, 1053 w, 933 m, 919 sh, 843 vw, 836 vw, 808 m, 773 vw
	B. (arene)$W(CO)_3$ Complexes		
$C_6H_6W(CO)_3$	1990 s, 1916 vs	3030 vw	1428 m, 1146 w, 1140 vw, 1135 w, 1004 w, 999 w, 962 w, 958 vw, 953 vw, 888 w, 773 m
$CH_3C_6H_5W(CO)_3$	1984 s, 1910 vs	3030 vw, 2880 vvw	1440 w, 1394 vw, 1376 w, 1291 vw, 1145 w, 1137 vw, 1055 vw, 1031 w, 1007 vw, 980 vw, 879 w, 796 w, 775 w
p-$(CH_3)_2C_6H_4W(CO)_3$	1978 s, 1906 vs	3020 vvw, 2860 vvw	1463 w, 1435 br, sh, 1377 m, 1350 vw, 1148 w, 1096 vw, 1028 w, 1007 vw, 829 vw, 807 w
s-$(CH_3)_3C_6H_3W(CO)_3$	1975 s, 1902 vs	3030 vw, 2880 vvw	1440 m, 1378 w, 1371 w, 1292 w, 1144 vw, 1030 m, 1005 w, 982 w, 865 w, 848 w
	C. (diene)$W(CO)_4$ Complexes		
1,5-$C_8H_{12}W(CO)_4$	2043 s, 1952 vs, 1907 vs	2910 w, 2860 vw, 2810 vw	1495 w, 1470 vw, 1448 w, 1437 w, 1331 w, 1324 vw, 1300 vw, 1240 vw, 1215 vw, 1190–1185 vw, br, 1167 w, 1087 vw, 1066 vw, 1015 vw, 985 w, 975 sh, 852 w, 824 vw, 809 w
$C_7H_8W(CO)_4$	2049 s, 1960 vs, 1914 vs	3050 vvw, 2960 vw, 2930 vvw, 2880 vvw	1440 vw, 1420 vw, 1413 vw, 1300 w, 1172 w, 1155 w, 1105 vw, 1076 w, 1069 vw, 1036 vw, 1005 vw, 975 vw, 923 w, 909 w, 895 w, 781 w
$C_{10}H_{12}W(CO)_4$	2045 s, 1959 vs, 1909 vs	2900 w, 2820 vw	1437 w, 1394 vw, 1321 vw, 1298 vw, 1257 vw, 1166 vw, 1131 vw, 1087 w, 1075 w, 1065 vw, 1046 vw, 984 w, 963 sh, 927 vw, 883 vw, 864 vw, 820 w, 773 vw, 714 vw
	D. (dienyl)$W(CO)_3H$ Complexes		
$C_5H_5W(CO)_3H$	2032 s, 1941 vs	3070 vw	1418 w, 1005 vw, 840 sh, 824 m
$C_5(CH_3)_5W(CO)_3H$	2015 s, 1928 vs	2920 w, 2820 w	1475 w, 1445 vw, 1379 m, 1028 w, 935 vw, 928 vw, 892 vw, 813 vw
	E. Other Complexes		
$(C_6H_8)_2W(CO)_2$	2000 s, 1952 s, 1920 m	2940 vw, 2890 sh, 2860 w, 2810 m	1465 m, 1440 w, 1426 vw, 1402 vw, 1381 vw, 1318 w, 1306 vw, 1251 w, 1224 w, 1165 m, 1133 w, 1103 vw, 1077 vw, 1060 vw, 1032 w, 1012 vw, 994 vw, 986 vw, 950 vw, 941 vw, 930 w, 894 w, 874 w, 845 w, 833 vw, 826 vw, 815 w, 803 w, 771 vw
$(CH_3COCH{=}CH_2)_3W$	None	3000 vw, 2900 w	1495 s, 1430 s, 1358 s, 1325 s, 1206 s, 1130 m, 1045 s, 1023 s, 982 s, 898 m, 882 s, 869 s, 858 vs, 786 s, 776 m
$[(CF_3)_2C_2]_3WNCCH_3$	None	2900 vvw	2280 vw,[f] 1725 m, 1286 s, 1210 vs, 1180 s, 1154 vs, 1125 vs, 978 m, 951 vw, 828 vw, 769 w, 697 m
$(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$	2004 m, 1870 vs, 1853 vs, 1837 m, 1822 s[c]	3000 sh, 2940 w, 2900 m	1460 s, 1437 s, 1400 m, 1284 vw, 1274 w, 1230 vw, 1182 vw, 1170 vw, 1155 vw, 1132 vw, 1111 w, 1090 vw, 1057 w, 1035 w, 1007 w, 988 w, 980 sh, 950 m, 925 w, 805 m, 768 m
$[C_7H_7W(CO)_3][BF_4]$	2060 s, 1980 s, 1905 s, 1820 s[b]	2980 w	1427 w, 1100 sh,[g] 1078 sh,[g] 1064 s,[g] 1034 s,[g] 862 vw, 814 vw, 805 vw, 721 w
$C_7H_7W(CO)_2I$	1995 vs, 1939 vs[c]	3000 vvw	1476 w, 1427 m, 1243 vw, 1177 vw, 1165 vw, 955 w, 927 m, 892 vw, 865 vw, 852 w, 803 s, 797 s
$C_5H_5W(CO)_2C_7H_7$	1967 s, 1958 s, 1910 s, 1893 s	3070 vw, 2975 w	1547 vw, 1447 vw, 1415 w, 1140 w, 1058 vw, br, 1002 vw, 923 vw, br, 879 vw, 837 m, 832 m, 716 m

TABLE III (*Footnotes*)

[a] Cyclohexane solutions on a Beckman IR-9 spectrometer unless otherwise indicated. [b] KBr pellets on a Perkin-Elmer Model 21 spectrometer. [c] Halocarbon oil mulls on a Beckman IR-9 spectrometer. [d] ν_{CC} of uncomplexed C_8H_8 double bond. [e] ν_{CN} of 6-dimethylaminofulvene ligand. [f] ν_{CN} of complexed acetonitrile. [g] ν_{BF} of BF_4^- anion.

two crops. These crystals have a very faint pink tinge like that of manganese(II) salts and a mousy odor like that of acetamide. *Anal.* Calcd for $C_{14}H_3F_{18}NW$: C, 23.6; H, 0.4; N, 2.0; F, 48.1; W, 25.9. Found: C, 23.4; H, 0.5; N, 2.3; F, 47.4; W, 25.1.

^{1}H Nmr Spectrum.—A sharp singlet resonance at τ 7.05 in chloroform solution due to the three equivalent methyl protons of the CH_3CN ligand.

^{19}F Nmr Spectrum.—Resonances at 57.6 and 60.5 ppm upfield from internal CCl_3F of equal relative intensities.

Preparation of $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$.—A mixture of 5.0 g (14.2 mmoles) of tungsten hexacarbonyl, 5.0 ml (4.5 g, 39 mmoles) of N,N,N′,N′-tetramethylethylenediamine, and 50 ml of cyclooctane was refluxed 30 hr with magnetic stirring. After cooling to room temperature, the yellow crystals that separated were washed with a few milliliters of pentane and dried. After drying at 70° (0.3 mm) for 3 hr to ensure removal of any unreacted tungsten hexacarbonyl (none appeared to be present), the crude product was recrystallized from a mixture of dichloromethane and hexane to give 5.43 g (93% yield) of yellow, crystalline $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$, mp 276–278° dec.

Upon heating about 20 hr with excess bicyclo[2.2.1]heptadiene or dicyclopentadiene in boiling hexane, the tungsten compound $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$ was recovered (>85%) unchanged. *Anal.* Calcd for $C_6H_{16}N_2O_4W$: C, 29.1; H, 3.9; N, 6.8; O, 15.5. Found: C, 28.8; H, 4.0; N, 6.7; O, 15.9.

Preparation of $[C_7H_7W(CO)_3][BF_4]$.—Filtered solutions of 7.2 g (20 mmoles) of cycloheptatriene tungsten tricarbonyl in ~100 ml of dichloromethane and of 7.2 g (21.8 mmoles) of triphenylmethyl tetrafluoroborate in ~100 ml of dichloromethane were mixed and stirred for 1 hr at room temperature. The resulting precipitate was filtered, washed with dichloromethane and diethyl ether, and dried to give 6.5 g (73% yield) of an orange powder. The analytical sample was recrystallized from a mixture of acetone and benzene. Upon heating above ~230° the orange crystals gradually became black. *Anal.* Calcd for $C_{10}H_7BF_4WO_3$: C, 26.9; H, 1.6; F, 17.0; W, 41.3. Found: C, 26.9; H, 1.6; F, 16.7; W, 41.0.

Preparation of $C_7H_7W(CO)_2I$.—A mixture of 6.0 g (13.5 mmoles) of $[C_7H_7W(CO)_3][BF_4]$, 6.0 g (40 mmoles) of sodium iodide, and 50 ml of CP acetone was stirred at room temperature. The reaction mixture immediately became dark brown but then green-black more gradually. After about 17 hr the acetone was removed at ~25° (30 mm). The residue was extracted with ~100 ml of dichloromethane in four portions. The filtered extracts were treated with ~25 ml of hexane and solvent was gradually removed at ~25° (30 mm). The crystals were washed on a filter with pentane and dried to give 5.47 g (88% yield) of green-black $C_7H_7W(CO)_2I$, mp 185–191° dec. The analytical sample was recrystallized an additional time from a dichloromethane–hexane mixture. *Anal.* Calcd for $C_9H_7IO_2W$: C, 23.6; H, 1.5; O, 7.0; I, 27.7. Found: C, 22.9; H, 1.6; O, 8.4; I, 28.2.

Preparation of $C_5H_5W(CO)_2C_7H_7$.—A solution of 40 mmoles of sodium cyclopentadienide in ~200 ml of redistilled tetrahydrofuran was treated with 4.0 g (8.73 mmoles) of $C_7H_7W(CO)_2I$. The reaction mixture was stirred for 15 hr at room temperature becoming orange. Solvent was then removed at ~25° (30 mm). The residue was extracted with three 100-ml portions of dichloromethane and solvent was removed from the filtered orange extracts at 25° (30 mm). A filtered solution of the orange residue in ~70 ml of benzene was chromatographed on a 2 × 50 cm alumina column. The chromatogram was developed with benzene and the single orange band was eluted with benzene. Solvent was removed from the filtered benzene eluate leaving orange crystals. These crystals were extracted with 100 ml of boiling hexane in three portions. The hexane extracts were filtered hot and the filtrate was concentrated to ~50 ml. Some orange crystals of the product precipitated. Cooling to −78° for 2 days precipitated more of the product which was filtered and dried to give 0.57 g (16.5% yield) of yellow-orange crystals, mp 111–117° dec. Purer product, mp 137–141° dec, could be obtained by sublimation at ~90° (0.1 mm) but the recovery of sublimed product was only ~10%. *Anal.* Calcd for $C_{14}H_{12}O_2W$: C, 42.4; H, 3.0; O, 8.1; W, 46.5. Found: C, 42.6; H, 3.1; O, 8.2; W, 46.2.

Proton Nmr Spectra. A. $C_7H_8W(CO)_3$.—Resonances at τ 3.87 (double doublet, $J_1 = 5$, $J_2 = 2$ cps), τ 5.12 (complex multiplet), and τ ~6.4 (complex multiplet—four asymmetric peaks) of approximate relative intensities 2:2:4 in CS_2 solution. The six complexed olefinic protons appear in three pairs at τ 3.87, 5.12, and 6.4. The two methylene protons overlap with the τ 6.4 resonance.

B. $C_8H_8W(CO)_3$.—Resonances at τ 3.84 (broad singlet), τ 4.5 (broad apparent doublet, separation ~11 cps), τ 4.7 (broad singlet), and τ 5.47 (broad apparent doublet, separation ~11 cps) of approximate relative intensities 2:2:2:2 in C_6H_5Br solution due to the two uncomplexed olefinic protons and the three nonequivalent pairs of complexed olefinic protons, respectively.

C. $C_7H_8W(CO)_4$.—Resonances at τ 5.37 (asymmetric triplet), τ 6.04 (broad singlet), and τ 8.92 (singlet) of approximate relative intensities 4:2:2 in CS_2 solution due to the four complexed olefinic protons, the two bridgehead protons, and the two bridge methylene protons, respectively.

D. $C_8H_{12}W(CO)_4$.—Resonances at τ 5.55 (broad singlet, width at half-height 7 cps) and τ 7.38 (broad singlet, width at half-height 5 cps) of approximate relative intensities 4:8 in CS_2 solution due to the four complexed olefinic protons and the eight protons of the four methylene groups, respectively.

E. $(C_6H_8)_2W(CO)_2$.—Resonances at τ 5.33 (double doublet, $J_1 = 6$, $J_2 = 3$ cps), τ 7.17 (broad singlet, width at half-height 12 cps), τ 7.91 (doublet of double doublets, $J_1 = 11$, $J_2 = 3$, $J_3 = 1$ cps), and τ 8.24 (doublet of double doublets, $J_1 = 11$, $J_2 = 3$, $J_3 = 1$ cps) of relative intensities 2:2:2:2 in CS_2 solution due to the two pairs of complexed olefinic protons and the two sets of methylene protons of the two equivalent 1,3-cyclohexadiene ligands, respectively.

F. $C_5(CH_3)_5W(CO)_3H$.—Resonances at τ 7.80 (singlet) and τ 16.85 (singlet) of approximate relative intensities 15:1 in CS_2 solution due to the 15 protons of the five equivalent methyl groups and the single proton directly bonded to the tungsten atom, respectively.

G. $(CH_3COCH{=}CH_2)_3W$.—Resonances at τ 5.77 (double doublet, $J_1 = 7$, $J_2 = 6$ cps), τ 7.87 (sharp singlet), and τ 8.4 (complex pattern—four apparent peaks) of relative intensities 1:3:2 in CS_2 solution due to the complexed vinyl proton adjacent to the ketonic carbonyl group, the three methyl protons, and the other two complexed vinyl protons of each of the three equivalent methyl vinyl ketone ligands.

H. $C_6H_6W(CO)_3$.—Single sharp resonance at τ 4.77 in CS_2 solution due to the six equivalent complexed aromatic protons.

I. $CH_3C_6H_5W(CO)_3$.—Resonances at τ 4.8 (complex pattern—five discernible asymmetric peaks) and τ 7.62 (sharp singlet) of approximate relative intensities 5:3 in CS_2 solution due to the five complexed aromatic protons and the three equivalent methyl protons, respectively.

J. *p*-$(CH_3)_2C_6H_4W(CO)_3$.—Resonances at τ 4.77 (sharp singlet) and τ 7.69 (sharp singlet) of approximate relative intensities 4:6 in CS_2 solution due to the four equivalent complexed aromatic protons and the six equivalent methyl protons, respectively.

K. 1,3,5-$(CH_3)_3C_6H_3W(CO)_3$.—Resonances at τ 5.10 (sharp singlet) and τ 7.59 (sharp singlet) of approximate relative intensities 3:9 in CS_2 solution due to the three equivalent complexed aromatic protons and the nine equivalent methyl protons, respectively.

L. $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$.—Resonances at τ 6.95 (singlet) and τ 7.13 (singlet) of approximate relative intensities 12:4 in $CHCl_3$ solution due to the 12 methyl protons and the four methylene protons, respectively.

M. $C_7H_7W(CO)_2I$.—Resonance at τ 4.63 (sharp singlet) in $CHCl_3$ solution due to the seven equivalent cycloheptatrienyl protons.

N. $C_5H_5W(CO)_2C_7H_7$.—Resonances at τ 4.79 (sharp singlet) and τ 5.29 (singlet) of approximate relative intensities 5:7 in CS_2 solution due to the five π-cyclopentadienyl protons and the seven π-cycloheptatrienyl protons, respectively.

Mass Spectra.[17] **A. $C_{10}H_{12}W(CO)_4$.**—The following ions with *m/e* >315 were observed: $C_{10}H_{12}W(CO)_4^+$ (*m/e* 428, relative intensity 34), $C_{10}H_{12}W(CO)_3^+$ (*m/e* 400, relative intensity 7), $C_{10}H_{12}W(CO)_2^+$ (*m/e* 372, relative intensity 16), $C_{10}H_{12}W(CO)^+$ (*m/e* 344, relative intensity 30), and $C_{10}H_{12}W^+$ (*m/e* 316, relative intensity 147).

B. $(C_6H_8)_2W(CO)_2$.—The following major ions with *m/e* >160 were observed: $(C_6H_8)_2W(CO)_2^+$ (*m/e* 400, relative intensity 39), $(C_6H_8)_2WCO^+$ (*m/e* 372, relative intensity 13), $C_6H_8W(CO)C_6H_6^+$ (*m/e* 370, relative intensity 20), $(C_6H_6)_2W^+$ (*m/e* 340, relative intensity 100), $C_6H_6W(CO)_2^+$ (*m/e* 318, relative intensity 18), $C_6H_6WCO^+$ (*m/e* 290, relative intensity 45), $C_6H_6W^+$ (*m/e* 262, relative intensity 61), and $(C_6H_6)_2W^{2+}$ (*m/e* 170, relative intensity 60).

C. $(CH_3COCH{=}CH_2)_3W$.—The following ions with *m/e* >300 were observed: $(CH_3COCH{=}CH_2)_3W^+$ (*m/e* 394, relative intensity 43), $(CH_3COCH{=}CH_2)_2W^+$ (*m/e* 324, relative intensity 100), and $CH_3COCH{=}CH_2WCH{=}CH_2CO^+$ (*m/e* 309, relative intensity 26). Further degradation appeared to involve rather complex rupture of the methyl vinyl ketone ligands.

D. $[(CF_3)_2C_2]_3W(NCCH_3)$.—The following ions with *m/e* >300 were observed: $(C_4F_6)_3WNCCH_3^+$ (*m/e* 711, relative intensity 80), $(C_4F_6)_2(C_4F_5)WNCCH_3^+$ (*m/e* 692, relative intensity 68), $(C_4F_6)_2(C_4F_5)W^+$ (*m/e* 651, relative intensity 15), $(C_4F_6)_2W(NCCH_3)F^+$ (*m/e* 568, relative intensity 280), $(C_4F_6)_2WNCCH_3^+$ (*m/e* 549, relative intensity 270), $(C_4F_6)_2W^+$ (*m/e* 508, relative intensity 92), $C_4F_6WC_4F_5^+$ (*m/e* 489, relative intensity 15), $C_4F_6W(NCCH_3)F_2^+$ (*m/e* 425, relative intensity 200), $C_{12}F_{14}^+$ (*m/e* 410, relative intensity 330), $C_{12}F_{13}H^+$ (*m/e* 392, relative intensity 420), $C_{12}F_{13}^+$ (*m/e* 391, relative intensity 430), $C_{12}F_{12}H^+$ (*m/e* 373, relative intensity 270), $C_{12}F_{12}^+$ (*m/e* 372, relative intensity 485), $C_{11}F_{11}^+$ (*m/e* 341, relative intensity 440), $C_{11}F_{10}H^+$ (*m/e* 323, relative intensity 520), $C_{11}F_{10}^+$ (*m/e* 322, relative intensity 290), and $(CH_3CN)WF_4^+$ (*m/e* 301, relative intensity 590).

E. $C_5H_5W(CO)_2C_7H_7$.—The following two ions with *m/e* >300 were observed: $C_5H_5W(CO)_2C_7H_7^+$ (*m/e* 396, relative intensity 11) and $C_5H_5WC_7H_7^+$ (*m/e* 340, relative intensity 44).

Ultraviolet and Visible Spectra.[18] **A. $C_7H_8W(CO)_3$.**—Maxima at 220 (22,000), 251 (14,700), 320 (10,500), and 494 (630) in cyclohexane solution (pale red-violet).

B. $C_8H_{10}W(CO)_3$.—Maxima at 222 (48,100), 275 (18,200), 318 (15,150), and 420 (910) in cyclohexane solution (orange).

C. $C_8H_8W(CO)_3$.—Maxima at 280 (11,800), 321 (10,270), and 460 (670) in cyclohexane solution (brown).

D. $C_5H_4CHN(CH_3)_2W(CO)_3$.—Maxima at 232 (11,200), 252 (9700), 317 (6200), and 437 (3100) in dichloromethane solution (red-yellow).

E. $C_6H_6W(CO)_3$.—Maximum at 316 (31,400) in dichloromethane solution (pale yellow).

F. $CH_3C_6H_5W(CO)_3$.—Maximum at 316 (26,400) in dichloromethane solution (pale yellow).

G. 1,4-$(CH_3)_2C_6H_4W(CO)_3$.—Maximum at 318 (34,300) in dichloromethane solution (pale yellow).

H. 1,3,5-$(CH_3)_3C_6H_3W(CO)_3$.—Maximum at 316 (24,500) in dichloromethane solution (pale yellow).

I. 1,5-$C_8H_{12}W(CO)_4$.—Maxima at 236 (40,300) and 275 (17,000) in cyclohexane solution (pale yellow).

J. $C_7H_8W(CO)_4$.—Maxima at 233 (36,200), 257 (20,000), and 274 (18,700) in cyclohexane solution (pale yellow).

K. $C_{10}H_{12}W(CO)_4$.—Maxima at 235 (38,300) and 278 (13,700) in cyclohexane solution (pale yellow).

L. $(C_6H_8)_2W(CO)_2$.—Maximum at 292 (7100) in cyclohexane solution (pale yellow).

M. $(CH_3COCH{=}CH_2)_3W$.—Maximum at 272 (9000) in cyclohexane solution (very pale yellow).

N. $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$.—Maxima at 220 (30,000), 254 (39,000), 298 (13,100), and 394 (1600) in dichloromethane solution (yellow).

O. $[(CF_3)_2C_2]_3W(NCCH_3)$.—No maxima observed in the 230–400-mμ region in cyclohexane or dichloromethane solutions (colorless).

P. $C_7H_7W(CO)_2I$.—Maxima at 232 (23,000), 276 (8800), 310 (7200), 387 (1230), 463 (430), and 665 (230) in dichloromethane solution (dark yellow-green).

Discussion

A. Complexes of the Type (triene)W(CO)$_3$.—The cycloheptatriene derivative, $C_7H_8W(CO)_3$, is obtained in only trace quantities from tungsten hexacarbonyl and cycloheptatriene analogous to the preparations of the chromium and molybdenum analogs $C_7H_8M(CO)_3$.[6b,19] It has been previously synthesized from the 1,5-cyclooctadiene complex $C_8H_{12}W(CO)_4$ and cycloheptatriene.[20] However, the synthesis from $(CH_3CN)_3W(CO)_3$ and cycloheptatriene reported here is far superior.

This new synthesis of $C_7H_8W(CO)_3$ has made it available for the first time in quantities sufficient for chemical studies. Triphenylmethyl tetrafluoroborate in dichloromethane solution abstracts hydride from $C_7H_8W(CO)_3$ to give the orange salt $[C_7H_7W(CO)_3][BF_4]$. Reaction of this salt with sodium iodide in acetone gives a brown solution which becomes green-black after a few hours at room temperature. From this green-black solution, the green-black, solid, covalent iodide $C_7H_7W(CO)_2I$ was isolated completely analogous to the known molybdenum analog $C_7H_7Mo(CO)_2I$.[3] The initial observation of a transient dark brown solution in the reaction between sodium iodide and $[C_7H_7W(CO)_3][BF_4]$ suggests appreciable stability of an intermediate tricarbonyl derivative possibly I which eventually loses one carbonyl group to give $C_7H_7W(CO)_2I$. A similar observation was not made in the more rapid reaction between sodium iodide and $[C_7H_7Mo(CO)_3][BF_4]$ consistent with the weaker molybdenum–carbon bonds.

The molybdenum compound $C_7H_7Mo(CO)_2I$ was previously[3b] shown to react with sodium cyclopentadienide to give orange $C_5H_5Mo(CO)_2C_7H_7$ for which the novel structure II (M = Mo) with an "allylic" π-cycloheptatrienyl ring was proposed despite the presence of only two sharp singlets in the proton nmr spectrum at room temperature corresponding to five equiva-

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(17) The ions containing tungsten in these mass spectra exhibited the expected multiline pattern owing to the presence of the following isotopes in natural tungsten: ^{180}W (0.14%), ^{182}W (26.29%), ^{183}W (14.31%), ^{184}W (30.66%), and ^{186}W (28.60%). The masses of the ions containing ^{184}W are reported in the spectra given here.

(18) Extinction coefficients are given in parentheses; wavelengths are in mμ.

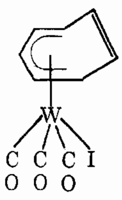
(19) E. W. Abel, M. A. Bennett, R. Burton, and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(20) T. A. Manuel and F. G. A. Stone, *Chem. Ind.* (London), 231 (1960).

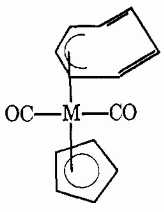
lent π-cyclopentadienyl protons and seven π-cycloheptatrienyl protons. Reaction between $C_7H_7W(CO)_2I$ and sodium cyclopentadienide gives a similar orange compound $C_5H_5W(CO)_2C_7H_7$ which likewise exhibits only two sharp singlets in its proton nmr spectrum at room temperature. The arguments already used for formulation of $C_5H_5Mo(CO)_2C_7H_7$ as II (M = Mo)[3b] may be similarly invoked for formulation of $C_5H_5W(CO)_2C_7H_7$ as II (M = W). In both $C_5H_5M(CO)_2C_7H_7$ compounds at $-40°$, the π-C_7H_7 but not the π-C_5H_5 resonance becomes much broader suggesting that at this low temperature the seven protons of the allylic π-cycloheptatrienyl groups are beginning to become nonequivalent as required for a "fixed" structure II.[21] A difficulty with the study of the tungsten compound $C_5H_5W(CO)_2C_7H_7$ was the inability to purify it by sublimation without extensive decomposition to a nonvolatile black substance. Thus $C_5H_5W(CO)_2C_7H_7$ appears to be relatively unstable thermally.

Fischer, Palm, and Fritz[22] reported tungsten hexacarbonyl to react with 1,3,5-cyclooctatriene to give only $(C_8H_{10})_2W(CO)_2$. No $C_8H_{10}W(CO)_3$ was obtained analogous to the chromium and molybdenum complexes $C_8H_{10}M(CO)_3$ (M = Cr and Mo). Thus the tungsten compound $C_8H_{10}W(CO)_3$, like $C_7H_8W(CO)_3$, is an example of a tungsten compound obtainable efficiently from $(CH_3CN)_3W(CO)_3$ but not directly from $W(CO)_6$. The proton nmr spectrum of $C_8H_{10}W(CO)_3$ was complex but qualitatively similar to that of $C_8H_{10}Mo(CO)_3$.[14]

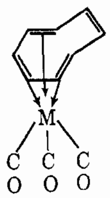
The compound $C_8H_8Mo(CO)_3$ (III, M = Mo) obtained by Winstein, Kaesz, Kreiter, and Friedrich[7] from (diglyme)$Mo(CO)_3$ and cyclooctatetraene has already been discussed. The tungsten compound $C_8H_8W(CO)_3$ appears to have the analogous structure III (M = W). Unlike its molybdenum analog, the tungsten compound $C_8H_8W(CO)_3$ exhibits a proton nmr spectrum at ambient temperature in which all four nonequivalent proton pairs are distinguishable. The eight C_8H_8 protons only become equivalent to nmr at temperatures much above room temperature.[21] The thermal stability of $C_8H_8W(CO)_3$ appears to be appreciably higher than that of $C_8H_8Mo(CO)_3$ consistent with the generally higher stability of tungsten–carbon bonds. Nevertheless, appreciable decomposition occurs upon sublimation of larger quantities.



I



II



III

The dimethylaminofulvene derivative $C_5H_4CHN(CH_3)_2W(CO)_3$ obtained from $(CH_3CN)_3W(CO)_3$ and dimethylaminofulvene appears to be IV (M = W) completely analogous to the previously reported[15] compounds $C_5H_4CHN(CH_3)_2M(CO)_3$ (IV, M = Cr or Mo) obtained from the corresponding metal hexacarbonyls and 6-dimethylaminofulvene. In the previous study,[15] the tungsten compound IV (M = W) could not be obtained from tungsten hexacarbonyl and 6-dimethylaminofulvene. Unfortunately $C_5H_4CHN(CH_3)_2W(CO)_3$ (IV, M = W) was too sparingly soluble, even in acetone-d_6, for a recognizable proton nmr spectrum to be obtained.

The arene–tungsten tricarbonyl compounds described in this paper have all been previously prepared[23,24] from tungsten hexacarbonyl and the aromatic hydrocarbon under appropriate conditions. However, the substitution of $(CH_3CN)_3W(CO)_3$ for tungsten hexacarbonyl permits much lower reaction temperatures and especially shorter reaction times suggesting that eventually aromatic compounds will be found which form arene–tungsten tricarbonyl complexes upon reaction with $(CH_3CN)_3W(CO)_3$ but not with tungsten hexacarbonyl. The arene–tungsten tricarbonyl compounds are less volatile and soluble than the tungsten tricarbonyl complexes of nonaromatic trienes of similar empirical formula (cycloheptatriene and 1,3,5-cyclooctatriene). Furthermore, the arene–tungsten tricarbonyl complexes are yellow whereas the tungsten tricarbonyl complexes of cycloheptatriene and 1,3,5-cyclooctatriene are red to orange. Finally, the arene–tungsten tricarbonyls exhibit a *sharp* maximum in the ultraviolet spectrum at 315–318 mμ (ϵ 24,000–32,000) unlike the tungsten tricarbonyl complexes of cycloheptatriene and 1,3,5-cyclooctatriene.

B. Complexes of the Type (diene)$W(CO)_4$.—Several examples have been encountered where nonconjugated dienes react with $(CH_3CN)_3W(CO)_3$ to give diene–tungsten *tetra*carbonyl derivatives. The extra mole of carbon monoxide must come from decomposition of some of the $(CH_3CN)_3W(CO)_3$. For such a reaction the yields of some of these diene–tungsten tetracarbonyl derivatives sometimes are remarkably good (*e.g.*, ~75% in two cases). The facile introduction of an extra carbon monoxide ligand in these cases may be related to the facile carbonylation of the *tri*carbonyls $C_8H_8Mo(CO)_3$ (C_8H_8 = cyclooctatetraene) and $C_8H_{10}Mo(CO)_3$ (C_8H_{10} = 1,3,5-cyclooctatriene) to give the tetracarbonyls $C_8H_8Mo(CO)_4$ and $C_8H_{10}Mo(CO)_4$, respectively, by carbon monoxide at atmospheric pressure and room temperature.[25]

The 1,5-cyclooctadiene complex $C_8H_{12}W(CO)_4$ has been obtained previously in reasonable (~52%) yield from tungsten hexacarbonyl and 1,5-cyclooctadiene, but in the high-boiling Soltrol solvent.[20] The bicycloheptadiene complex $C_7H_8W(CO)_4$ is obtainable only in very low yields from tungsten hexacarbonyl and bicycloheptadiene.[6b] The syntheses of these diene

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[21] The temperature dependence of the proton nmr spectra of these compounds will be discussed in a future publication.

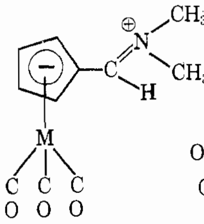
[22] E. O. Fischer and C. Palm, *Z. Naturforsch.*, **14b**, 347 (1959); E. O. Fischer, C. Palm, and H. P. Fritz, *Ber.*, **92**, 2645 (1959).

[23] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *ibid.*, **91**, 2763 (1958).

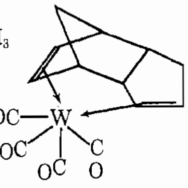
[24] W. Strohmeier, *Z. Naturforsch.*, **17b**, 566 (1962).

[25] H. D. Kaesz, S. Winstein, and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966).

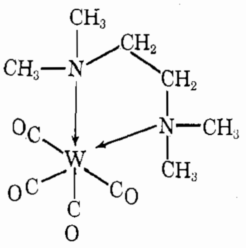
complexes from $(CH_3CN)_3W(CO)_3$ and the appropriate diolefin appear advantageous.



IV



V



VI

The dicyclopentadiene complex $C_{10}H_{12}W(CO)_4$ (V) is the first metal carbonyl complex of dicyclopentadiene where it acts as a chelating diolefin, as in the dicyclopentadiene–metal dihalides of palladium and platinum.[26] The only metal carbonyl complex of dicyclopentadiene reported in the literature is $C_5H_5Mn(CO)_2C_{10}H_{12}$ where only one double bond is π bonded to the metal atom.[27] In general, metal carbonyls react with dicyclopentadiene only at higher temperatures where dedimerization occurs to form cyclopentadiene which may then form a cyclopentadienylmetal carbonyl. Unfortunately, the low yield of $C_{10}H_{12}W(CO)_4$ prevented a detailed study of this compound.

The low yield of $C_{10}H_{12}W(CO)_4$ obtained from dicyclopentadiene and $(CH_3CN)_3W(CO)_3$ and the inability to obtain characterizable quantities of a tungsten tetracarbonyl complex of 1,5-hexadiene from $(CH_3CN)_3W(CO)_3$ and 1,5-hexadiene suggested a search for a tungsten carbonyl intermediate with *four* carbonyl groups bonded to the tungsten atom and only *two* positions occupied with ligands with no $p\pi$–$d\pi$ bonding ability. This intermediate might form (diene)$W(CO)_4$ compounds more readily with appropriate dienes than $(CH_3CN)_3W(CO)_3$ since addition of an extra carbonyl group is not required. In this connection tungsten hexacarbonyl and N,N,N′,N′-tetramethylethylenediamine react in boiling cyclooctane to give a good yield of bright yellow crystalline $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$ (VI). Unfortunately, the nitrogen ligands in VI were not readily replaced with chelating diolefins in boiling hexane solution. Thus $(CH_3)_2NCH_2CH_2N(CH_3)_2W(CO)_4$ (VI) was recovered unchanged after heating with bicycloheptadiene or dicyclopentadiene for several hours in boiling hexane. Possibly the chelating nature of the N,N,N′,N′-tetramethylethylenediamine ligands and its lower basicity relative to acetonitrile account for its firmer bonding to the tungsten atom.

C. Reaction between $(CH_3CN)_3W(CO)_3$ and Conjugated Dienes. No products other than small amounts of tungsten hexacarbonyl were obtained from attempted reactions of $(CH_3CN)_3W(CO)_3$ with acyclic dienes such as butadiene or 2,3-dimethylbutadiene or acyclic trienes such as 1,3,5-hexatriene or alloocimene. Only with the cyclic conjugated dienes, cyclopentadiene and 1,3-cyclohexadiene, were olefin complexes obtained in appreciable quantities by reaction with $(CH_3CN)_3W(CO)_3$. Only negligible quantities of tungsten carbonyl compounds (mainly $W(CO)_6$) were obtained from reactions of $(CH_3CN)_3W(CO)_3$ with 1,3-cycloheptadiene and 1,3-cyclooctadiene.

Cyclopentadiene reacts with $(CH_3CN)_3W(CO)_3$ to give the known[28] hydride $C_5H_5W(CO)_3H$. Apparently the hydrogen atom lost by the cyclopentadiene to give the π-C_5H_5 ligand becomes attached to the tungsten atom. The formation of a relatively unstable cyclopentadienylmetal carbonyl hydride from reactions between pure metal carbonyls and cyclopentadiene has been postulated as an intermediate step in the formation of cyclopentadienylmetal carbonyls from metal carbonyls and cyclopentadiene.[29] This reaction between $(CH_3CN)_3W(CO)_3$ and cyclopentadiene is the first example of such a reaction where the hydride derivative is sufficiently stable under the reaction conditions to be isolated as the principal product.

The reaction of $(CH_3CN)_3W(CO)_3$ with pentamethylcyclopentadiene proceeds with more difficulty than the corresponding reaction with unsubstituted cyclopentadiene. Apparently the hydrogen atom in pentamethylcyclopentadiene is transferred to the tungsten atom with considerably more difficulty—as a consequence of this the reaction between $(CH_3CN)_3W(CO)_3$ and pentamethylcyclopentadiene was best carried out in boiling methylcyclohexane (bp 101°) rather than the boiling hexane (bp 65°) more frequently used for reactions involving $(CH_3CN)_3W(CO)_3$. The presence of a single hydrogen atom bonded directly to the tungsten atom in $C_5(CH_3)_5W(CO)_3H$ was confirmed by observation of a high-field proton nmr resonance at τ 16.85. The compound $C_5(CH_3)_5W(CO)_3H$ is the first reported metal carbonyl complex of pentamethylcyclopentadiene although other such compounds such as $C_5(CH_3)_5Mo(CO)_3H$, $[C_5(CH_3)_5Mo(CO)_3]_2$, $[C_5(CH_3)_5Fe(CO)_2]_2$, and $C_5(CH_3)_5Co(CO)_2$ have been prepared in this laboratory[16] but not yet reported in the literature. The only reported π-pentamethylcyclopentadienyl derivative is the titanium compound $C_5(CH_3)_5TiCl_3$.[30]

1,3-Cyclohexadiene reacts with $(CH_3CN)_3W(CO)_3$ in a still different manner giving $(C_6H_8)_2W(CO)_2$ apparently entirely analogous to the molybdenum complex $(C_6H_8)_2Mo(CO)_2$ obtained by Fischer and Fröhlich[31] from 1,3-cyclohexadiene and molybdenum hexacarbonyl. The proton nmr spectrum of $(C_6H_8)_2W(CO)_2$ confirmed the expected structure VII (M = W) with two equivalent π-cyclohexadiene ligands.

A characteristic property of the molybdenum com-

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[26] K. A. Hofmann and J. von Narbutt, *Ber.*, **41**, 1625 (1908); J. R. Doyle and H. B. Jonassen, *J. Am. Chem. Soc.*, **78**, 3965 (1956); J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).

[27] Reference 4, p 109.

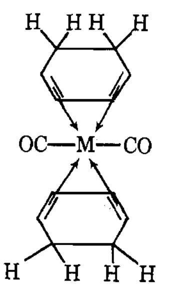
[28] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956); E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. Anorg. Allgem. Chem.*, **282**, 47 (1955).

[29] H. W. Sternberg and I. Wender, "Papers Presented at the International Conference on Coordination Chemistry, London, April 1959," Chemical Society Special Publication 13, The Chemical Society, London, 1960, p 41.

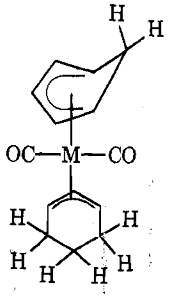
[30] H. Röhl, E. Lange, T. Gössl, and G. Roth, *Angew. Chem.*, **74**, 155 (1962).

[31] E. O. Fischer and W. Fröhlich, *Z. Naturforsch.*, **15b**, 266 (1960); H. P. Fritz, H. Keller, and E. O. Fischer, *Naturwissenschaften*, **48**, 518 (1961).

plex $(C_6H_8)_2Mo(CO)_2$ is its conversion at ~100° to the isomeric $C_6H_7Mo(CO)_2C_6H_9$ (VIII, M = Mo) by means of a hydrogen shift from one C_6H_8 ligand to the other. An analogous compound was not obtained by heating $(C_6H_8)_2W(CO)_2$ (VII, M = W) in boiling 2,2,5-trimethylhexane for 14 hr. Instead a 59% recovery of $(C_6H_8)_2W(CO)_2$ was obtained and identified as pure VII (M = W) on the basis of its melting point, infrared spectrum, and proton nmr spectrum. Thus hydrogen migration in $(C_6H_8)_2W(CO)_2$ (VII, M = W) occurs with much more difficulty than in the molybdenum analog. Furthermore, hydride removal from $(C_6H_8)_2W(CO)_2$ with triphenylmethyl hexafluorophosphate in dichloromethane solution was slow and incomplete. The yellow precipitate was obtained in insufficient quantity for characterization.



VII

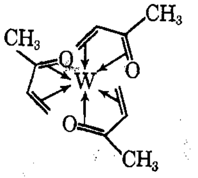


VIII

D. The Compound $(CH_3COCH{=}CH_2)_3W$.—The molybdenum derivative $(CH_3CN)_3Mo(CO)_3$ is reported to react with methyl vinyl ketone to give an orange solid of composition $[(CH_3COCH{=}CH_2)_2Mo(CO)_2]_n$.[32] The reaction between $(CH_3CN)_3W(CO)_3$ and methyl vinyl ketone to give yellow, volatile, air-stable $(CH_3COCH{=}CH_2)_3W$ with complete loss of all carbonyl and acetonitrile ligands was thus completely unexpected.

The spectroscopic properties of this unusual complex are of interest. The positive ion mass spectrum exhibits a strong ion at *m/e* 394 corresponding to the molecular ion $(CH_3COCH{=}CH_2)_3W^+$ followed by a strong ion at *m/e* 324 corresponding to $(CH_3COCH{=}CH_2)_2W^+$ with loss of one methyl vinyl ketone fragment. Further fragmentation is more complex. The infrared spectrum exhibits no bands in the usual regions for ν_{CO} of either metal carbonyl or ketonic carbonyl groups. A strong band at 1495 cm^{-1} may arise from ν_{CO} of a complexed ketonic group. This drastic modification of the ν_{CO} frequency suggests that the carbon–oxygen double bonds of the $CH_3COCH{=}CH_2$ ligands are π complexed to the tungsten atom in $(CH_3COCH{=}CH_2)_3W$. The proton nmr spectrum exhibits resonances at τ 5.72 (double doublet, $J_1 = 6$, $J_2 = 7$ cps), τ 7.87 (singlet), and τ 8.4 (complex multiplet) of relative intensities 1:3:2, respectively, due to the vinyl proton adjacent to the (ketonic) carbonyl group, the three methyl protons, and the two remaining "terminal" vinyl protons of each of the three equivalent $CH_3COCH{=}CH_2$ ligands. The large difference between the chemical shifts of these vinyl protons and those of usual types of vinyl protons around τ 4 indicates that the carbon–carbon double bonds of the $CH_3COCH{=}CH_2$ ligands are π complexed to the tungsten atom in $(CH_3COCH{=}CH_2)_3W$.

Since both the carbon–carbon and carbon–oxygen double bonds of each of the three equivalent $CH_3COCH{=}CH_2$ ligands appear to be bonded to the tungsten atom, the complex $(CH_3COCH{=}CH_2)_3W$ must have structure IX. In this structure the tungsten atom is hexacoordinate tungsten(0) as in $W(CO)_6$ itself.[33] The bonding of the $CH_3COCH{=}CH_2$ ligand to the tungsten atom in $(CH_3COCH{=}CH_2)_3W$ is probably similar to that of the cinnamaldehyde ligand to the iron atom in the complex $(C_6H_5CH{=}CHO)Fe(CO)_3$.[34] This cinnamaldehyde complex, like $(CH_3COCH{=}CH_2)_3W$, is reported to exhibit no ν_{CO} bands in the normal ketonic carbonyl region.



IX

E. The Compound $[(CF_3)_2C_2]_3W(NCCH_3)$.—Recently the reaction between hexafluorobutyne-2 and nickel tetracarbonyl was reported to give the novel tetranuclear complex $[(CF_3)_2C_2]_3Ni_4(CO)_3$.[35] The presence of two ^{19}F nmr resonances of equal relative intensities suggests that the three hexafluorobutyne-2 ligands are equivalent but that the two ends of each ligand are nonequivalent.

The three alkyne ligands in the complexes (alkyne)$_3$W(CO) are likewise equivalent but each alkyne ligand has nonequivalent ends.[12] The reaction between $(CH_3CN)_3W(CO)_3$ and hexafluorobutyne was investigated in an attempt to obtain the analogous complex $[(CF_3)_2C_2]_3W(CO)$. However, the air-stable, white, crystalline, volatile product was $[(CF_3)_2C_2]_3W(NCCH_3)$ confirmed by a molecular ion at *m/e* 711 in its mass spectrum.

The proton nmr spectrum of this new complex exhibits a singlet resonance at τ 7.05 owing to the three methyl protons of the complexed acetonitrile ligand. The ^{19}F nmr spectrum exhibits two resonances of equal relative intensities indicating that the three hexafluorobutyne-2 ligands are equivalent but that the two ends of each ligand are nonequivalent. This complex $[(CF_3)_2C_2]_3W(NCCH_3)$ thus appears to be closely related to the (alkyne)$_3$W(CO) complexes but with a lone acetonitrile ligand instead of a lone carbonyl ligand.

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(32) D. P. Tate, A. A. Buss, J. M. Augl, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965).

(33) Alternatively, the methyl vinyl ketone ligands can be considered as a delocalized system similar to butadiene donating four electrons to the tungsten atom.

(34) K. Stark, J. E. Lancaster, H. D. Murdoch, and E. Weiss, *Z. Naturforsch.*, **19b**, 284 (1964).

(35) R. B. King, M. I. Bruce, J. R. Phillips, and F. G. A. Stone, *Inorg. Chem.*, **5**, 684 (1966).

Apparently the ligand remaining after displacement of five of the six ligands in $(CH_3CN)_3W(CO)_3$ with three alkyne ligands depends on the nature of the alkyne. The electronegative CF_3 groups of the hexafluorobutyne-2 ligands may withdraw d electrons from the tungsten atom in $[(CF_3)_2C_2]_3WL$ complexes to the extent that insufficient electron density remains for stabilization of a tungsten–carbonyl bond by partial $p\pi$–$d\pi$ multiple bonding. Thus the ligand remaining attached to the tungsten atom in the hexafluorobutyne complex is the acetonitrile ligand which does not require any $p\pi$–$d\pi$ multiple bonding to form stable bonds with transition metals.

Acknowledgment.—We are indebted to Mr. M. B. Bisnette for assistance with the pressure reactions and other special experiments. We are indebted to the U. S. Air Force Office of Scientific Research for partial support under Grants AF-AFOSR-580-64 and AF-AFOSR-580-66. We also appreciate the generous samples of cyclooctatetraene provided by the Badische Anilin- und Soda-Fabrik, Ludwigshafen, Germany, for this and related research.

Contribution from the Chemistry Division, Research Department,
U. S. Naval Ordnance Test Station, China Lake, California 93555

Acid Decomposition of Tetraalkyl-2-tetrazenes in Aqueous Solution[1]

By WILLIAM R. McBRIDE and WAYNE E. THUN

Received May 16, 1966

Kinetics for the decomposition of the conjugate acid of tetraalkyl-2-tetrazene homologs was studied, principally by spectrophotometric techniques. Rate data establish the effect of acidity, tetraalkyl-2-tetrazene concentration, temperature, and ionic strength upon the first-order reaction in aqueous solution. A linear free energy relationship was observed between the pK_b values determined for the tetraalkyl-2-tetrazenes and the rate constants for the acid decomposition. Arrhenius constants are nearly the same for the tetraalkyl-2-tetrazenes examined.

Introduction

The reaction for the decomposition of 1,1,4,4-tetraalkyl-2-tetrazenes in acid solution was postulated by Renouf[2] and Fischer and Troschke[3] according to the equation

$$R_2NN{=}NNR_2 + H_2O \xrightarrow{\text{acid}} R_2NH + RNH_2 + R'CHO + N_2 \qquad (1)$$

for the methyl and ethyl homologs, respectively. In eq 1 R′ represents the next lower homolog of R. Overberger and Marks[4] supported the general acid decomposition scheme for 2-tetrazenes described by Wieland and Fressel[5] which considered the initial formation of the secondary amine, nitrogen, and a decomposition fragment which subsequently hydrolyzed to give the primary amine and aldehyde. Although decomposition products were characterized for the above reaction and the stoichiometry established by nitrogen evolution, the kinetics for the acid decomposition has not been reported. Since evidence for the formation of the conjugate acid of a tetraalkyl-2-tetrazene from the corresponding 1,1-dialkyldiazenium ion, $R_2N^+{=}NH$, and its conjugate base in acid solution has been published,[6] we have undertaken a detailed study of the acid decomposition of a homologous series of tetraalkyl-2-tetrazenes, derivatives of an unsaturated hydronitrogen with type formula N_4H_4.[7] In this paper we present the kinetic data for the reaction.

Experimental Section

Materials.—Methods previously described for the preparation and reduction of dialkylnitrosamines[8] with lithium aluminum hydride in ether[9] and the oxidation of the corresponding 1,1-dialkylhydrazines with yellow mercuric oxide or potassium bromate[6] were used to prepare the tetraalkyl-2-tetrazenes. The 2-tetrazenes were purified by vacuum distillation from barium oxide and occasionally by gas–liquid partition chromatography;[6] the purity as estimated by ultraviolet spectra or gas–liquid partition chromatograms was 97–100%. All other materials used were reagent grade chemicals available commercially.

Kinetic Measurements.—The acid decomposition of tetraalkyl-2-tetrazenes in aqueous solution was followed principally by spectrophotometric measurements in the ultraviolet region. Glass-stoppered, 100-ml volumetric flasks nearly filled with the appropriate aqueous solution were equilibrated in a water or oil bath maintained within ±0.05° of the desired temperature. After the appropriate 2-tetrazene in ethanol or water was added to each flask, the solution was diluted to volume and equilibrated at the bath temperature with good agitation for 10–20 min before the initial absorbance, A_0, was measured. During these studies the initial 2-tetrazene concentration was approximately $2 \times 10^{-4}\ M$ with the pH adjusted to about 2. The limited solubility of the higher homologs of the tetraalkyl-2-tetrazenes in

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(1) Presented in part before the Division of Inorganic Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) E. Renouf, *Ber.*, **13**, 2169 (1880).

(3) E. Fischer and H. Troschke, *Ann.*, **199**, 294 (1879).

(4) C. G. Overberger and B. S. Marks, *J. Am. Chem. Soc.*, **77**, 4097 (1955).

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(6) W. R. McBride and E. M. Bens, *J. Am. Chem. Soc.*, **81**, 5546 (1959).

(7) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, pp 3–6.

(8) For a review of carcinogenic effects ascribed to nitrosamines see J. H. Weisburger and E. K. Weisburger, *Chem. Eng. News*, **44**, No. 6, 124 (1966).

(9) H. Zimmer, L. F. Audrieth, M. Zimmer, and R. A. Rowe, *J. Am. Chem. Soc.*, **77**, 790 (1955).