

Preparation and Reactions of Alkyl- and Arylpentacarbonyltungsten Anions

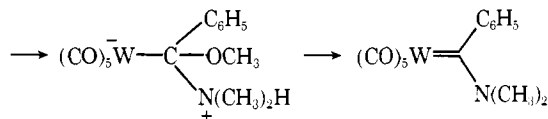
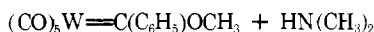
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Abstract: Photolysis of $(\text{CO})_5\text{WCOR}^-$ leads to loss of CO and formation of $(\text{CO})_5\text{WR}^-$. Reaction of RLi with $(\text{CO})_5\text{WBr}^-$ also gives $(\text{CO})_5\text{WR}^-$ species. Reaction of $(\text{CO})_5\text{WR}^-$ with HCl leads to protonation of the carbon-metal bond and formation of RH . Treatment of $(\text{CO})_5\text{WR}^-$ with CO or with $\text{P}(\text{C}_6\text{H}_5)_3$ leads to carbonyl insertion products when $\text{R} = \text{CH}_3$ or C_6H_5 but not when $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$.

Introduction

The reactions of group 6 metal carbene complexes with nucleophiles proceed via nucleophilic attack at the electron-deficient carbene carbon atom to produce a tetravalent carbon intermediate. The tetravalent carbon intermediates have been



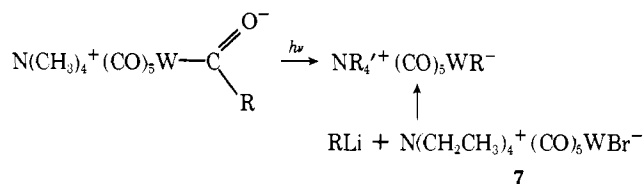
isolated from reactions of carbene complexes with phosphines,¹ 1,5-diazabicyclo[2.2.2]octane,² and trimethoxyborohydride.³ Similar intermediates have been proposed in the reactions of alkoxy-substituted carbene complexes with amines,⁴ thiols,⁵ and alkoxides⁶ which lead to new nitrogen, sulfur, and oxygen substituted carbene complexes. Organolithium compounds attack alkoxy-substituted carbene complexes at the carbene carbon atom to give unisolated intermediates which were subsequently converted to non-heteroatom-stabilized carbene complexes.⁷ The reactions of alkoxy-substituted carbene complexes with phosphoranes⁸ and with diazoalkanes⁹ were proposed to proceed via initial nucleophilic attack at the carbene carbon atom followed by extrusion of vinyl ethers.

To give further insight into the nature and reactivity of these intermediates, we set out to synthesize methyl-, phenyl-, and benzylpentacarbonyltungsten anions.¹⁰ Prior to the beginning of the work reported here, $(\text{CO})_5\text{MCF}=\text{CF}_3^-$,¹¹ $(\text{CO})_5\text{MC}\equiv\text{CC}_6\text{H}_5^-$,¹² $(\text{CO})_5\text{CrC}(\text{OCH}_3)=\text{CH}_2^-$,¹³ and $(\text{CO})_5\text{MC}\equiv\text{N}^-$ ^{11,14} were the only known $(\text{CO})_5\text{MX}^-$ species where $\text{X} = \text{carbon}$. More recently, Ellis and Hagen have reported the isolation of alkylpentacarbonylchromium and tungsten anions from the reaction of $\text{M}(\text{CO})_5^{2-}$ with alkyl halides.¹⁵

Results and Discussion

Synthesis of $(\text{CO})_5\text{WR}^-$. Two synthetic routes to $(\text{CO})_5\text{WR}^-$ were explored. The photolysis of acyl tungsten species led to the expulsion of CO and migration of the organic group to the metal. Alternatively, the reaction of organolithium reagents with $(\text{CO})_5\text{WBr}^-$ was found to give $(\text{CO})_5\text{WR}^-$ species. The highest yields of $(\text{CO})_5\text{WR}^-$ were obtained by photolysis when R was benzyl and by reaction of the tungsten halide with RLi when R was methyl or phenyl.

Photolysis of an acetone- d_6 solution of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCOCH}_3^-$ (**1**) with 350-nm light was monitored by ¹H NMR. The signal for the acetyl methyl group of **1** at δ 2.30 disappeared within 2 h and a new signal appeared at δ -0.74 which was attributed to $(\text{CO})_5\text{WCH}_3^-$. The chemical shift of the methyltungsten anion is shifted approximately 0.5 ppm to higher field than the neutral $(\text{CO})_5\text{ReCH}_3$.¹⁷ A 15% yield of



- | | |
|--|---|
| 1, R = CH ₃ | 8m, R = CH ₃ ; R' = CH ₃ |
| 2, R = C ₆ H ₅ | 8e, R = CH ₃ ; R' = CH ₂ CH ₃ |
| 3, R = C ₆ H ₄ - <i>m</i> -CH ₃ | 9m, R = C ₆ H ₅ ; R' = CH ₃ |
| 4, R = C ₆ H ₄ - <i>p</i> -CH ₃ | 9e, R = C ₆ H ₅ ; R' = CH ₂ CH ₃ |
| 5, R = CH ₂ C ₆ H ₅ | 10m, R = C ₆ H ₄ - <i>m</i> -CH ₃ ; R' = CH ₃ |
| 6, R = CH ₂ C ₆ H ₄ - <i>p</i> -CH ₃ | 11m, R = C ₆ H ₄ - <i>p</i> -CH ₃ ; R' = CH ₃ |
| | 11e, R = C ₆ H ₄ - <i>p</i> -CH ₃ ; R' = CH ₂ CH ₃ |
| | 12m, R = CH ₂ C ₆ H ₅ ; R' = CH ₃ |
| | 12e, R = CH ₂ C ₆ H ₅ ; R' = CH ₂ CH ₃ |
| | 13m, R = CH ₂ C ₆ H ₄ - <i>p</i> -CH ₃ ; R' = CH ₃ |

$\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_3^-$ (**8m**) was isolated from the photolysis solution.

The reaction of methyl lithium with $\text{NEt}_4^+(\text{CO})_5\text{WBr}^-$ (**7**) resulted in the immediate precipitation of lithium bromide. Addition of 1 N sodium hydroxide (high pH enhanced the aqueous stability of **8e**) and removal of THF gave $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_3^-$ (**8e**) in 84% yield. **8e**, a bright yellow, crystalline compound, is moderately air sensitive in the solid state and is rapidly air oxidized in solution. The infrared spectrum of **8e** has four metal carbonyl bands at 2036 (w), 1926 (w), 1887 (s), and 1848 (m) cm^{-1} characteristic of a metal pentacarbonyl anion.¹⁸ The IR bands are assigned to the three IR-active fundamental vibrations ($2A_1 + E$) expected for a C_{4v} metal pentacarbonyl species and to the B_1 vibration which is IR inactive for rigorous C_{4v} geometry.

Reaction of phenyllithium with **7** gave an 80% yield of $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WC}_6\text{H}_5^-$ (**9e**) isolated as a moderately air-sensitive, yellow, crystalline material. Photolysis of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCOC}_6\text{H}_5^-$ (**2**) in a sealed NMR tube for 20 h in acetone gave the corresponding tetramethylammonium salt, **9m**, in 25% isolated yield. The NMR spectrum of **9e** in the aromatic region consisted of a two-proton multiplet at δ 7.84 assigned to the ortho protons and a three-proton multiplet at δ 6.77. This assignment was confirmed by analysis of the 270-MHz NMR spectrum of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WC}_6\text{H}_4\text{-}m\text{-CH}_3^-$ (**10m**), which also exhibited two low-field ortho protons at δ 7.63 (d, $J = 7.2$ Hz) and 7.71 (s). The large downfield shift of the ortho protons of **9e** is analogous to that observed for $(\text{CO})_5\text{ReC}_6\text{H}_5$ ¹⁹ and other MC_6H_5 compounds.²⁰

Photolysis of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCOCH}_2\text{C}_6\text{H}_5^-$ (**5**) for 6 h in acetone with nitrogen passing through the solution gave a 50% yield of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_2\text{C}_6\text{H}_5^-$ (**12m**). Reaction of benzylmagnesium chloride with $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WBr}^-$ (**7**) gave the corresponding tetraethylammonium salt, **12e**, in 15% yield. The aromatic region of the NMR spectrum of **12m** consists of a four-proton multiplet at δ 6.9–7.0

and a complex multiplet at δ 6.49 assigned to the para proton. This assignment was confirmed by comparison with the NMR spectrum of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_2\text{C}_6\text{H}_4\text{-}p\text{-CH}_3^-$ (**13m**), which has a four-proton multiplet at δ 6.76 and no absorption near δ 6.5. The upfield NMR shift of the para proton of σ -bonded benzyltungsten anions appears to be a general effect and has also been observed for $(\text{CO})_5\text{WC}(\text{OCH}_3)(\text{C}_6\text{H}_5)\text{-CH}_3^-$ ²² and for $(\text{CO})_5\text{WCH}(\text{OCH}_3)\text{C}_6\text{H}_5^-$.³

The photolytic decarbonylation of acyltungsten anions used in one of our routes to $(\text{CO})_5\text{WR}^-$ compounds is analogous to the photolytic decarbonylations of neutral and cationic acyl-metal compounds previously reported.^{23,24} Corresponding thermal decarbonylations have, of course, been thoroughly investigated.²⁴

The reaction of $(\text{CO})_5\text{WBr}^-$ with organolithium reagents used in our other route to $(\text{CO})_5\text{WR}^-$ compounds is analogous to reactions of Grignard or lithium reagents with $(\text{CO})_5\text{-MnBr}$ ²⁵⁻²⁷ and *cis*- $[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})_4\text{ReBr}$.²⁸ While this work was in progress, the synthesis of silyl-, germyl, and stannyl-pentacarbonylmetalates of Cr, Mo, and W by a similar route was reported.²⁹ The reaction of triphenylsilyllithium with $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{CrCl}^-$ at room temperature in THF gave $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{CrSi}(\text{C}_6\text{H}_5)_3^-$ in 82% yield. The reaction works well for a large number of main group 4 anions.

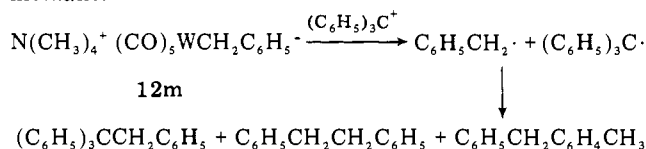
Recently, an alternative route to alkylpentacarbonylmetalate anions of Cr and W was reported.¹⁵ The reaction of $\text{M}(\text{CO})_5^{2-}$ with an alkyl halide results in the displacement of halide and the formation of the alkyl metal anion. The preparation of methyl-, ethyl-, benzyl-, and cyanomethylpentacarbonylmetalate anions of Cr and W was successful by this procedure. However, aryl tungsten anions are not available via this route.

Reactions of $(\text{CO})_5\text{WR}^-$ with Electrophiles. Treatment of $(\text{CO})_5\text{WR}^-$ salts with anhydrous HCl results in instantaneous liberation of the protonated alkyl or aryl ligand. Reaction of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_2\text{C}_6\text{H}_5^-$ (**12m**) with HCl gave toluene (94%) and $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCl}^-$ (77%). Similarly, reaction of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WC}_6\text{H}_4\text{-}p\text{-CH}_3^-$ (**11m**) with HCl gave toluene (84%) and reaction of **8e** with HCl gave methane. The related reaction of $(\text{CO})_5\text{ReCH}_3$ with $\text{CF}_3\text{CO}_2\text{H}$ results in vigorous methane evolution.³⁰ Reaction of $(\text{CO})_5\text{-WSi}(\text{C}_6\text{H}_5)_3^-$ with HCl gives $(\text{C}_6\text{H}_5)_3\text{SiH}$.²⁹ Rather than undergoing cleavage of the carbon-metal bond, α -methoxybenzylpentacarbonyltungsten anions react with acids via protonation of the methoxy group and cleavage of the carbon-oxygen bond to give methanol and neutral carbene complexes.^{7,22,31}

The reactions of benzoyl chloride with $(\text{CO})_5\text{WR}^-$ gave phenyl ketones in low to moderate yields. Reaction of $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_3^-$ (**8e**) with benzoyl chloride gave acetophenone (24%). Similarly, $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{-WC}_6\text{H}_5^-$ (**9e**) reacted with benzoyl chloride to give benzophenone (42%). Ellis and Hagen have reported that $[(\text{PPh}_3)_2\text{N}]^+(\text{CO})_5\text{WCH}_2\text{C}_6\text{H}_5^-$ does not react with benzyl chloride or other alkyl halides after 18 h at room temperature.¹⁵ However, they did observe rapid reactions of $(\text{CO})_5\text{-WR}^-$ with $(\text{C}_6\text{H}_5)_3\text{SnCl}$ and with $(\text{C}_6\text{H}_5)_3\text{PAuCl}$.¹⁵

The reaction of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_2\text{C}_6\text{H}_5^-$ (**12m**) with trityl cation was investigated as a possible route to $(\text{CO})_5\text{-WCHC}_6\text{H}_5$.³ The preparation of carbene complexes by hydride abstraction with $(\text{C}_6\text{H}_5)_3\text{C}^+$ has been reported.³² The reaction of **12m** with $(\text{C}_6\text{H}_5)_3\text{C}^+\text{BF}_4^-$ occurs in CH_2Cl_2 at -78°C . The major reaction product was 1,1,1,2-tetraphenylethane (52%); in addition, small amounts of 1,2-diphenylethane and of phenyl-*p*-tolylmethane were also isolated. Apparently, trityl cation reacts with **12m** via an electron transfer mechanism which leads to formation of trityl and benzyl radicals. Coupling of a trityl and a benzyl radical leads to

formation of 1,1,1,2-tetraphenylethane. Coupling of benzyl radicals leads to 1,2-diphenylethane. Attack of a benzyl radical at the para position of **12m** could lead to phenyl-*p*-tolylmethane.³³



Reactions of $(\text{CO})_5\text{WR}^-$ with CO and $\text{P}(\text{C}_6\text{H}_5)_3$. The reaction of CO or $\text{P}(\text{C}_6\text{H}_5)_3$ with $(\text{CO})_5\text{WR}^-$ led to facile formation of acyl species when R was methyl or aryl but no acyl species was observed when R was benzyl. The methyl compound, **8m**, was the most reactive in CO insertion reactions. **8m** was completely converted to $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WCOCH}_3^-$ in 2 days at room temperature under 1 atm of CO. Reaction of 1 equiv of $\text{P}(\text{C}_6\text{H}_5)_3$ with **8m** proceeded to completion in 15 min at room temperature to give $\text{N}(\text{CH}_2\text{CH}_3)_4^+ \text{cis-}(\text{CO})_4\text{-}[\text{P}(\text{C}_6\text{H}_5)_3]\text{WCOCH}_3^-$.³⁴ Under similar conditions, the phenyl compound, **9e**, reacted more slowly to give CO insertion products. The reaction of **9e** with $\text{P}(\text{C}_6\text{H}_5)_3$ was complete in about 7 days. To confirm the structural assignments made for the insertion products with CO and PPh_3 , the resulting acyl anions were converted to their corresponding carbene complexes by methylation with $\text{CH}_3\text{OSO}_2\text{F}$.³⁵

In contrast, the benzyl anion, **12m**, gave no indication of the formation of insertion products with PPh_3 after 6 days at room temperature. Heating the reaction mixture to 60°C for 2 h gave $(\text{CO})_5\text{WP}(\text{C}_6\text{H}_5)_3$ ³⁶ (54%) and small amounts of *cis*- and *trans*- $(\text{CO})_4\text{W}[\text{P}(\text{C}_6\text{H}_5)_3]_2$.³⁷

The CO insertion reactions of $(\text{CO})_5\text{WR}^-$ are analogous to the reactions of $(\text{CO})_5\text{MnR}$ compounds. For example, both $(\text{CO})_5\text{MnCH}_3$ and $(\text{CO})_5\text{MnC}_6\text{H}_5$ undergo CO insertion but $(\text{CO})_5\text{MnCH}_2\text{C}_6\text{H}_5$ does not.³⁸ In agreement with the eight times greater reactivity of $(\text{CO})_5\text{MnCH}_3$ compared with $(\text{CO})_5\text{MnC}_6\text{H}_5$,³⁹ the methyltungsten anion undergoes much more rapid CO insertion than the phenyltungsten anion. In contrast, while $\text{N}(\text{CH}_2\text{CH}_3)_4^+[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})_4\text{WCOC}_6\text{H}_5^-$ is stable, the corresponding initially formed manganese species readily decarbonylates to *cis*- $[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})_4\text{MnC}_6\text{H}_5$.⁴⁰

Experimental Section

General. All reactions involving organometallic reagents were carried out in flame-dried glassware under a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium and benzophenone under nitrogen. Other solvents were either purged with nitrogen or degassed on a vacuum line ($<10^{-3}$ mmHg) prior to use. Solutions were transferred by syringe or cannula (hypodermic tubing) under positive nitrogen pressure. ¹H NMR spectra were recorded on a Jeolco MH-100, Varian XL-100, or Bruker WH-270 spectrometer. Chemical shifts for both ¹H and ¹³C spectra are reported in δ downfield from tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 267 spectrophotometer in the solvent specified. Mass spectra were recorded on an AEI-903 mass spectrometer at 70 eV. Analytical vapor phase chromatography was carried out on either a Hewlett-Packard 5750 or 5700 A gas chromatograph with flame ionization detector and either disk integrator or Hewlett-Packard 3380A integrator-recorder.

$\text{N}(\text{CH}_3)_4^+[(\text{CO})_5\text{WCOC}_6\text{H}_5]^-$ (**2**) was prepared as described by Fischer.¹⁶ Reaction of $\text{C}_6\text{H}_5\text{Li}$ (17.6 mL, 25 mmol, 1.42 M in benzene-ether) with $\text{W}(\text{CO})_6$ (8.8 g, 25 mmol) in 150 mL of ether gave **2** which was recrystallized from CH_2Cl_2 -ether to give red-orange crystals (7.78 g, 62%): NMR (acetone-*d*₆) δ 3.36 (12 H, s), 7.16–7.60 (5 H, m); IR (THF) ν_{CO} 2041 (w), 1952 (w), 1905 (s), 1885 (m) cm^{-1} .

Photolysis of $\text{N}(\text{CH}_3)_4^+[(\text{CO})_5\text{WCOCH}_3]^-$ (1**).** Acetone-*d*₆ (0.3 mL) was distilled into an NMR tube containing **1** (0.167 g, 0.38 mmol) on a vacuum line. The NMR tube was sealed and irradiated in a Srinivasan-Griffin photochemical reactor with a circular array of 16 General Electric F8T5/BLB lamps which have maximum emission at 350 nm and which emit greater than 97% of their energy between

300 and 400 nm. In acetone, **1** has absorption maxima at 362 nm ($\log \epsilon$ 3.46) and at 330 (3.54); acetone cuts off all radiation of higher energy than 317 nm. After 2 h irradiation, the absorption at δ 2.30 for the acyl methyl group was absent while a new absorption at δ -0.74 had appeared. The NMR tube was opened, and solvent was evaporated under reduced pressure. The residue was recrystallized twice from CH_2Cl_2 -ether to give **8m** (0.025 g, 15%) as a pale yellow, crystalline solid: NMR (acetone- d_6) δ -0.74 (3 H, s), 3.19 (12 H, s); IR (THF) ν_{CO} 2036 (w), 1926 (w), 1887 (s), 1848 (m) cm^{-1} .

Photolysis of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCOCH}_2\text{C}_6\text{H}_5^-$ (5**).** A solution of **5** (0.158 g, 0.306 mmol) in acetone- d_6 was photolyzed in an NMR tube. After 4 h, the absorption at δ 3.97 for the starting material was absent and a new absorption at δ 2.0 (partially obscured by the acetone- d_6 multiplet) was apparent in the NMR spectrum.

In a larger scale preparation, a solution of **5** (2.241 g, 4.343 mmol) in 50 mL of acetone was irradiated for 6 h with a slow stream of dry nitrogen passing through the solution to provide mixing. Solvent was evaporated under vacuum and the residue was recrystallized twice from CH_2Cl_2 -ether to give **12m** as light yellow crystals (0.99 g, 47%): NMR (acetone- d_6) δ 2.01 (2 H, s), 3.32 (12 H, s), 6.38–6.60 (1 H, m), 6.90–7.00 (4 H, m); IR (THF) ν_{CO} 2036 (w), 1937 (w), 1893 (s), 1846 (m) cm^{-1} ; ^{13}C NMR (acetone- d_6 , 0.07 M in $\text{Cr}(\text{acac})_3$) δ 4.7 ($\overline{\text{WCH}_2^-}$), 56.6 (1:1:1 triplet, $J = 4.2$ Hz, CH_3N^+), 118.4, 125.2, 127.6, 162.7 (phenyl carbons). The metal carbonyl carbons were obscured by the carbonyl carbon of acetone. On the basis of an undecoupled spectrum, the absorption at 162.7 ppm was assigned to the ipso carbon of the phenyl ring. The absorption at 118.4 ppm was assigned to the para carbon on the basis of its intensity ($1/2$ of those at 125.2 and 127.6 ppm).

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_5\text{W}$: C, 39.28; H, 3.91; N, 2.86; W, 37.58. Found: C, 39.14; H, 3.96; N, 2.83; W, 37.63.

$\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WBr}^-$ (7**)** was prepared by a modification of the procedure of Abel.¹⁸ $\text{W}(\text{CO})_6$ (4.5 g, 12.8 mmol) and $\text{N}(\text{CH}_2\text{CH}_3)_4^+\text{Br}^-$ (2.1 g, 10 mmol) in 50 mL of diglyme were heated to 120 °C for 14 h. Solvent and excess $\text{W}(\text{CO})_6$ were evaporated under reduced pressure. The residual yellow solid was dissolved in 20 mL of CH_2Cl_2 and 5 mL of acetone and filtered. Addition of hexane until crystallization began and cooling to -20 °C gave bright yellow **7** (5.04 g, 94%): IR (THF) ν_{CO} 2068 (w), 1955 (w), 1918 (s), 1859 (m) cm^{-1} .

$\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_3^-$ (8e**).** Methylolithium (2.56 mL, 3.90 mmol, 1.52 M in ether) was added to a solution of **7** (2.00 g, 3.75 mmol) in 40 mL of THF at room temperature. Aqueous NaOH solution (10 mL, 1 N) was added and the THF removed under reduced pressure. The suspended yellow granular solid was collected by filtration, dried in vacuo, and recrystallized from CH_2Cl_2 -hexane to give **8e** (1.48 g, 84%): ^1H NMR (acetone- d_6) δ -0.75 (3 H, s), 1.40 (12 H, tt, $J = 7.4$, $J_{\text{NH}} = 1.8$ Hz), 3.48 (8 H, q, $J = 7.4$ Hz); ^{13}C NMR (acetone- d_6 , 0.07 M in $\text{Cr}(\text{acac})_3$) δ -31.8 ($\overline{\text{WCH}_3}$), 9.9 ($^+\text{NCH}_2\text{CH}_3$), 55.3 ($^+\text{NCH}_2^-$); IR (THF) ν_{CO} 2036 (w), 1926 (w), 1887 (s), 1848 (m) cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{NO}_5\text{W}$: C, 35.84; H, 4.94; W, 39.18. Found: C, 35.70; H, 4.87; W, 38.95.

$\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WC}_6\text{H}_5^-$ (9e**)** was prepared by reaction of $\text{C}_6\text{H}_6\text{Li}$ (2.66 mL, 4.0 mmol, 1.5 M in benzene/ether) with **7** (2.0 g, 3.75 mmol) in 40 mL of THF. Workup similar to that used for **8e** gave yellow, crystalline **9e** (1.59 g, 80%). The infrared and NMR spectra for **9e** were similar to those exhibited by **9m**. ^{13}C NMR (acetone- d_6 , 0.07 M in $\text{Cr}(\text{acac})_3$): δ 9.7 ($^+\text{NCH}_2\text{CH}_3$), 54.9 ($^+\text{NCH}_2^-$), 123.5, 128.6, 150.6, 163.3 (phenyl carbons). Based on an undecoupled spectrum, the absorption at 163.3 ppm was assigned to the ipso carbon of the phenyl ring. The absorption at 123.5 ppm was tentatively assigned to the para carbon on the basis of intensity data.

Anal. Calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_5\text{W}$: C, 42.96; H, 4.74; W, 34.61. Found: C, 42.55; H, 4.67; W, 35.46.

Reactions of HCl with $(\text{CO})_5\text{WR}^-$. A solution of **8e** (0.10 g, 0.21 mmol) in 1 mL of THF was placed in a test tube equipped with a tight-fitting septum. A slight excess of dry HCl in ether was added. Vigorous gas evolution occurred immediately. The mixture was cooled to -78 °C and the gas above the solution analyzed by GC using a 2-m column of 3% Apiezon N on activated alumina (60/80) at room temperature. Methane was the only gaseous product eluted and was identified by comparison with the retention time of an authentic sample. Solvent was evaporated under reduced pressure and the residue recrystallized from CH_2Cl_2 -hexane to give $\text{N}(\text{CH}_2\text{CH}_3)_4^+(\text{CO})_5\text{WCl}^-$ (**18**) (0.06 g, 60%).

A slight excess of dry HCl in ether was added to a solution of **12m**

(0.34 g, 0.69 mmol) and *n*-nonane (as internal standard) in 5 mL of CH_2Cl_2 at room temperature. The resulting solution was analyzed directly by GC using a 6 ft \times $1/8$ in. UCW-98 (Chromosorb P 60/80) column at 50 °C. A 94% yield of toluene was determined. Solvent was evaporated under vacuum and residue recrystallized from CH_2Cl_2 -hexane to give $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCl}^-$ (0.23 g, 77%).

An excess of HCl in ether was added to **11e** (0.052 g, 0.096 mmol). An 84% yield of toluene was determined by GC as described above.

Reactions of $\text{C}_6\text{H}_5\text{COCl}$ with $(\text{CO})_5\text{WR}^-$. Benzoyl chloride (0.098 g, 0.70 mmol) was added to a solution of **8e** (0.322 g, 0.70 mmol) in 5 mL of THF at room temperature. After 30 min, the reaction mixture was analyzed by GC (1.25 m, 20% Carbowax 20M column, 180 °C, $\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_3\text{CH}_3$ internal standard). A 24% yield of acetophenone (identified by comparison of GC retention time) was determined.

Similarly, reaction of $\text{C}_6\text{H}_5\text{COCl}$ (0.098 g, 0.70 mmol) with **9e** (0.365 g, 0.70 mmol) gave a 42% yield of benzophenone (identified by comparison of GC retention times on a 5.5 ft, 20% SE-30 column at 215 °C, $(\text{C}_6\text{H}_5\text{CH}_2)_2$ internal standard).

Reaction of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCH}_2\text{Ph}^-$ (12m**) with $\text{Ph}_3\text{C}^+\text{BF}_4^-$.** Triphenylmethyl tetrafluoroborate (0.218 g, 0.66 mmol) in 5 mL of CH_2Cl_2 was added to a solution of **12m** (0.324 g, 0.66 mmol) in 8 mL of CH_2Cl_2 at -78 °C. As the solution warmed to room temperature, the color changed from light orange to red-brown. Analysis of the reaction mixture by TLC (90:10 hexane/ CH_2Cl_2) showed no elutable colored products; the presence of $\text{W}(\text{CO})_6$, $\text{Ph}_3\text{CCH}_2\text{Ph}$, $\text{PhCH}_2\text{CH}_2\text{Ph}$ (trace), Ph_3CH , and Ph_3COH was shown by comparison with authentic samples. Preparative thin layer chromatography (90:10 hexane/ CH_2Cl_2 ; silica gel) gave, after four elutions, $\text{Ph}_3\text{CCH}_2\text{Ph}$ (52%), $\text{PhCH}_2\text{CH}_2\text{Ph}$, and *p*- $\text{CH}_3(\text{C}_6\text{H}_4)\text{CH}_2\text{Ph}$, and small amounts of Ph_3COH and Ph_3CH . These compounds were identified by comparison of NMR spectra with spectra of authentic samples.

Reactions of CO with $(\text{CO})_5\text{WR}^-$. CD_2Cl_2 was distilled into an NMR tube containing **8e** (0.030 g, 0.064 mmol) on a vacuum line. With the sample at -78 °C, CO (640 mmHg) was introduced into the vacuum line and the NMR tube was sealed. After 2 days at room temperature, the absorption at δ -0.74 for the methyl anion had disappeared and a new absorption at δ 2.30 assigned to $(\text{CO})_5\text{WCOCH}_3^-$ was observed in the ^1H NMR. In a separate experiment, the $(\text{CO})_5\text{WCOCH}_3^-$ anion obtained by reaction of **8e** with CO in CD_2Cl_2 was methylated with $\text{CH}_3\text{OSO}_2\text{F}$ to give $(\text{CO})_5\text{WC}(\text{OCH}_3)\text{CH}_3$ in 59% yield.

Similarly, the ^1H NMR of a CD_2Cl_2 solution of **9e** sealed under 640 mm CO indicated greater than 80% conversion to $(\text{CO})_5\text{WCOC}_6\text{H}_5^-$ after 7 days at room temperature. In a separate experiment, $(\text{CO})_5\text{WCOC}_6\text{H}_5^-$ obtained by reaction of **9e** with CO was methylated with $\text{CH}_3\text{OSO}_2\text{F}$ to give $(\text{CO})_5\text{WC}(\text{OCH}_3)\text{C}_6\text{H}_5$ in 42% yield.

No change in the ^1H NMR of a CD_2Cl_2 solution of **12m** sealed under 640 mm CO was noted after 7 days at room temperature. Heating to 60 °C for 2 h resulted in partial decomposition (solid precipitation) but no ^1H NMR resonances attributable to $(\text{CO})_5\text{WCOCH}_2\text{C}_6\text{H}_5^-$ were observed.

Reactions of $\text{P}(\text{C}_6\text{H}_5)_3$ with $(\text{CO})_5\text{WR}^-$. A solution of **8e** (93 mg, 0.20 mmol) and $\text{P}(\text{C}_6\text{H}_5)_3$ (57 mg, 0.22 mmol) in 0.3 mL of CD_2Cl_2 was sealed in an NMR tube at -78 °C. Within approximately 15 min at room temperature **8e** had been completely converted to the acyl anion *cis*- $\text{PPh}_3(\text{CO})_4\overline{\text{WCOCH}_3}$ (3-proton singlet at δ 2.07).

Similarly, **9e** reacted with $\text{P}(\text{C}_6\text{H}_5)_3$ in CD_2Cl_2 to give greater than 95% $\text{PPh}_3(\text{CO})_4\overline{\text{WCOCH}_3}$ after 7 days at room temperature.

In contrast, **12m** gave no evidence by NMR for the formation of the corresponding acyl anion after 6 days at room temperature.

In a preparative scale reaction, **8e** (0.313 g, 0.667 mmol) and PPh_3 (0.192 g, 0.734 mmol) were dissolved in CH_2Cl_2 and the resulting solution was stirred at room temperature for 7 h. The solvent was removed on a rotary evaporator, and the residue methylated by the addition of $\text{CH}_3\text{OSO}_2\text{F}$ (60 μL) at -78 °C. Preparative TLC purification gave *cis*- $[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})_4\overline{\text{WC}(\text{OCH}_3)\text{CH}_3}$ (0.187 g, 46%) as an orange, crystalline solid which was identified by comparison of IR and NMR spectra with those of an authentic sample.³⁴

Similarly, the reaction of **9e** with PPh_3 for 7 days at room temperature gave, after methylation with $\text{CH}_3\text{OSO}_2\text{F}$, $[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})_4\overline{\text{WC}(\text{OCH}_3)\text{C}_6\text{H}_5}$ as a dark purple, crystalline solid: NMR (acetone- d_6) δ 4.36 (3 H, s, $\text{CH}_3\text{O}-$), 7.00–7.60 (20 H, m); IR (hexane) ν_{CO} 1930 (sh), 1925 (m), 1897 (s) cm^{-1} . The IR and NMR spectra were identical with the spectra of material prepared by the reaction

of PhLi with $(\text{CO})_5\text{WPPH}_3$ followed by methylation with $\text{CH}_3\text{O-SO}_2\text{F}$.

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Supplementary Material Available: The synthesis and IR and NMR spectra of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCOR}^-$ species **1**, **3**, **4**, **5** and **6**; the photolysis of $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WCOR}^-$ species, **2**, **3**, **4**, and **6**; the IR and NMR spectra of the $\text{N}(\text{CH}_3)_4^+(\text{CO})_5\text{WR}^-$ products **9m**, **10m**, **11m**, and **13m**; and the preparation and spectra of **11e** and **12e** (3 pages). Ordering information is given on any current masthead page.

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Reactions of the Excited States of Substituted Polypyridinechromium(III) Complexes with Oxygen, Iron(II) Ions, Ruthenium(II) and -(III), and Osmium(II) and -(III) Complexes

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Abstract: The series of complexes CrL_3^{3+} where L is a bipyridine or phenanthroline derivative has been used to investigate the mechanism of the quenching of the luminescence of $^*\text{CrL}_3^{3+}$ by O_2 , $\text{Fe}_{\text{aq}}^{2+}$, RuL_3^{2+} , $\text{Os}(\text{bpy})_3^{2+}$, $\text{Ru}(\text{bpy})_3^{3+}$, and $\text{Os}(\text{bpy})_3^{3+}$ in aqueous solution at 25 °C. The rate constants for the quenching of the $^*\text{CrL}_3^{3+}$ emission by O_2 are insensitive to the reduction potential of the chromium(III) complex. It is concluded that the reaction with O_2 is by energy transfer. The $^*\text{CrL}_3^{3+}$ emission is quenched much more efficiently by $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Os}(\text{bpy})_3^{2+}$ than by $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Os}(\text{bpy})_3^{3+}$. The rate constants for the quenching of the $^*\text{CrL}_3^{3+}$ emission by RuL_3^{2+} , $\text{Os}(\text{bpy})_3^{2+}$, and $\text{Fe}_{\text{aq}}^{2+}$ are sensitive to the reduction potential of the chromium(III) complex with the quenching by $\text{Fe}_{\text{aq}}^{2+}$ showing a linear relation between the logarithm of the quenching rate constant and the reduction potential. The ruthenium(II) and osmium(II) complexes show a more complex behavior with the quenching rate constant increasing less rapidly with driving force than is expected on the basis of the Marcus model. The rate constant for the $\text{CrL}_3^{2+}-^*\text{CrL}_3^{3+}$ exchange is estimated as $1 \times 10^8 \cdot \text{M}^{-1} \text{s}^{-1}$ in 1.0 M sulfuric acid at 25 °C and is compared with the corresponding ground-state exchange rate. The relation between ground- and excited-state exchange rates and Stokes shifts is discussed.

There is currently considerable interest in the reactions of the excited states of metal complexes.¹⁻⁶ This interest derives in part from the use of these complexes in model systems for the study of the conversion and storage of solar energy.^{7,8} An

additional reason for this interest is that the electron transfer reactions of excited states can be very exothermic and consequently such reactions can be used to test the predictions of theoretical models in the so-called inverted region.⁹