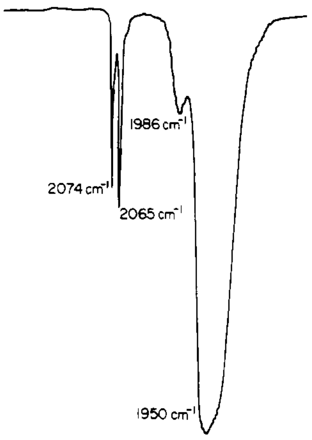

Figure 1. Carbonyl region of the infrared spectrum of $(OC)_5CrPPh_2CH_2CH_2PPh_2Mo(CO)_5$.

with $(OC)_5WPPh_2CH{=}CH_2$ and $(OC)_5CrPPh_2H$ or with $(OC)_5CrPPh_2CH{=}CH_2$ and $(OC)_5WPPh_2H$ as starting materials. The method should be very useful for preparing a variety of bis(tertiary phosphine)-bridged complexes.

The carbonyl regions of the infrared spectra of the three symmetrical complexes $(OC)_5WL{-}LW(CO)_5$, $(OC)_5MoL{-}LMo(CO)_5$, and $(OC)_5CrL{-}LCr(CO)_5$ show bands expected for pentacarbonyl moieties of C_{4v} symmetry. The E and $A_1^{(1)}$ modes overlap as is often observed for monosubstituted group 6 carbonyl complexes.[10] The mixed-metal complex $(OC)_5MoL{-}LW(CO)_5$ gives rise to a spectrum in which molybdenum carbonyl absorptions cannot be distinguished from those of the tungsten carbonyls. Since the $A_1^{(1)}$ modes of $(OC)_5WL{-}LW(CO)_5$ and $(OC)_5MoL{-}LMo(CO)_5$ absorb at 2073 and 2075 cm^{-1}, respectively, resolution of these individual absorptions in $(OC)_5MoL{-}LW(CO)_5$ would not be expected. For both $(OC)_5CrL{-}LMo(CO)_5$ and $(OC)_5CrL{-}LW(CO)_5$, however, resolution of the two $A_1^{(1)}$ modes is achieved, consistent with the difference of approximately 9 cm^{-1} between the $A_1^{(1)}$ absorption for $(OC)_5CrL{-}LCr(CO)_5$ and that of either the analogous molybdenum or tungsten complex (Figure 1). The overlapping E modes were not resolved for any of the mixed-metal complexes.

The ^{31}P NMR spectra of the mixed-metal complexes show chemical shifts downfield from phosphoric acid in the order $Cr > Mo > W$ as has been observed for simpler systems.[10] The two different phosphorus environments give rise to splitting due to phosphorus–phosphorus coupling. In addition tungsten-183–phosphorus-31 coupling is observed in the spectra of the tungsten complexes.

The ^{31}P NMR spectrum of $(OC)_5WL{-}LW(CO)_5$ is of special interest (Figure 2). The 14.28% abundant tungsten-183 is distributed such that the $(OC)_5{}^{183}WL{-}L^{183}W(CO)_5$, $(OC)_5{}^{183}WL{-}LW(CO)_5$, and $(OC)_5WL{-}LW(CO)_5$ distribution is 2.03, 24.48, and 73.48%, respectively. The satellite pattern observed in Figure 2 arises from $(OC)_5{}^{183}WL{-}LW(CO)_5$. This molecule, which contains two nonequivalent phosphorus nuclei as a result of the tungsten-183 isotope, gives rise to an ABX spectrum. The AB portion of the spectrum consists of two ab subspectra indicated by lines 1, 2, 4, and 6 and by lines 3, 5, 7, and 8. The recently reported NMR analysis of $Ph_2P(^{77}Se)CHCHP(Se)Ph_2$ parallels that for the tungsten complex exactly.[11] The value of $^1J_{WP}$ extracted from this spectrum is 241.6 Hz which is the same as was observed directly in the spectra of the two mixed dimetallic tungsten complexes. Within the limit of measurement (±0.2 Hz), the value for $^4J_{WP}$ is zero.

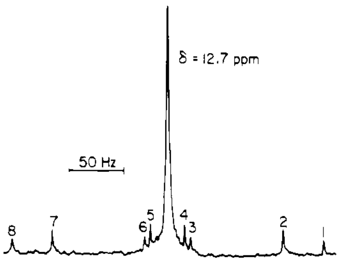

Figure 2. ^{31}P NMR spectrum of $(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$.

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Registry No. $(OC)_5MoPPh_2CH_2CH_2PPh_2W(CO)_5$, 75365-60-5; $(OC)_5MoPPh_2CH_2CH_2PPh_2Cr(CO)_5$, 75365-61-6; $(OC)_5MoPPh_2CH_2CH_2PPh_2Mo(CO)_5$, 14489-09-9; $(OC)_5WPPh_2CH_2CH_2PPh_2Cr(CO)_5$, 75365-62-7; $(OC)_5WPPh_2CH_2CH_2PPh_2W(CO)_5$, 15413-06-6; $(OC)_5CrPPh_2CH_2CH_2PPh_2Cr(CO)_5$, 15024-28-9; $(OC)_5WPPh_2CH{=}CH_2$, 64012-10-8; $(OC)_5CrPPh_2CH{=}CH_2$, 72868-75-8; $(OC)_5MoPPh_2CH{=}CH_2$, 75365-63-8; $(OC)_5CrPPh_2H$, 18399-60-5; $(OC)_5MoPPh_2H$, 18399-61-6; $(OC)_5WPPh_2H$, 18399-62-7.

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Convenient Preparation and Isolation of Pure Potassium Cyclopentadienyldicarbonylferrate, $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$

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Recently developed procedures for the cleavage of metal carbonyl dimers circumvent the need for hazardous, cumbersome reducing agents such as sodium amalgam[1,2] or sodium potassium alloy.[3] Potassium hydride[4] and certain trialkylborohydrides[5] efficiently reduce $[Mn(CO)_5]_2$, $[Co(CO)_4]_2$, and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ in THF solution at room temperature to afford $Mn(CO)_5^-$, $Co(CO)_4^-$, and $(\eta^5\text{-}C_5H_5)Mo(CO)_3^-$ in nearly quantitative yield. However, when either of these reagents is employed for the cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$, sluggish reaction rates are encountered unless a highly coordinating cosolvent such as hexamethylphosphoramide is used with THF. A sodium dispersion in THF serves as a cleavage reagent which has been employed for the in situ preparation of derivatives of $Na[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$.[13] Since complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]R$[6] (where R = allyl, alkyl) can promote a variety of useful transformations in organic molecules, it is of interest to develop a convenient technique for cleaving $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ which will also yield an isolable salt that can later be used as a stoichiometric reagent under a variety of conditions.

We find that potassium benzophenone ketyl rapidly and cleanly reduces $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ in THF at room tem-

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perature. After filtration and washing, pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ is obtained as a solvent-free, free-flowing solid in 75–80% yield. No evidence for the presence of other, more highly reduced species was found.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + 2K[(C_6H_5)_2CO] \xrightarrow{\text{THF}} 2K[(\eta^5\text{-}C_5H_5)Fe(CO)_2] + 2(C_6H_5)_2CO$$

This work represents the first reported isolation of a simple alkali metal salt of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ ion, although two salts with complex counterions, $[(C_4H_9)_4N][(\eta^5\text{-}C_5H_5)Fe(CO)_2]$[3] and $[(\eta^5\text{-}C_5H_5)Fe(CO)dmpe][(\eta^5\text{-}C_5H_5)Fe(CO)_2]$[7] (dmpe = 1,2-bis(dimethylphosphino)ethane), have previously been isolated.

Pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ is a yellow-orange, powdery solid which can be stored under nitrogen for a period of at least several months with no apparent loss of purity. Exposure of solid $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ to air results in the formation of purple $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ within several minutes. The solution infrared spectrum (THF) of the $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ isolated in this report is in good agreement with literature values.[3] As a Nujol mull, $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ exhibits two broad carbonyl bands at 1880 and 1735 cm^{-1}.

Previous uses of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ have involved generation of the anion in situ and subsequent addition of appropriate reagents to effect a desired reaction.[1,2] We anticipate that prior preparation and storage of pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ would save time and permit very precise control of reaction stoichiometries. Furthermore, choice of reaction solvents and temperatures[8] would no longer need to be limited by conditions required for the initial cleavage of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Experimental Section

All operations were performed on a standard high-vacuum system[9] or under an atmosphere of prepurified nitrogen. Benzophenone (J. T. Baker Chemical Co.) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ (Strem Chemical Co.) were used as received. Elemental potassium (Mallinckrodt Chemical Co.) was washed free of mineral oil with pentane and stored under nitrogen in a sealed vessel in a nitrogen filled drybox. *Caution! Potassium metal can form peroxides and superoxides even when stored under mineral oil if there is an atmosphere of air above the liquid.*[10] Therefore, we opened and sealed the bottle containing potassium under mineral oil only in the drybox. Tetrahydrofuran (THF) was initially distilled from $LiAlH_4$ and stored over sodium benzophenone ketyl. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer using matched 0.1-mm KBr cells. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Potassium benzophenone ketyl was prepared by magnetically stirring 3.64 g (20 mmol) of benzophenone and 0.78 g (20 mmol) of small, freshly cut pieces of potassium metal in 20 mL of dry THF. Typically, this mixture was stirred overnight to ensure complete solubilization of the potassium metal. Addition of 3.89 g (11 mmol, 10% excess) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to the rapidly stirred ketyl solution resulted in disappearance of the characteristic deep blue color of the potassium benzophenone within minutes and formation of a red solution and an orange precipitate.[11] The orange precipitate was isolated by vacuum-line filtration.[12] While still on the vacuum-line filter, the precipitate was washed repeatedly with benzene to free it of benzophenone and unreacted $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ to yield 3.22 g (74.5% yield) of analytically pure $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$. Anal. Calcd for $C_7H_5FeO_2K$: C, 38.89; H, 2.34; Fe, 25.86; K, 18.10. Found: C, 39.09; H, 2.61; Fe, 25.83; K, 17.95.

Acknowledgment. We thank the National Science Foundation for support of this work through Grant No. CHE79-18148.

Registry No. $K[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$, 60039-75-0; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9; potassium benzophenone ketyl, 19333-28-9; benzophenone, 119-61-9.

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Reactions of Coordinated Dinitrogen. 7.[1] Preparation and Characterization of Molybdenum Bis(dinitrogen) Complexes Containing Mixed Tertiary Phosphine Ligands[2]

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The notable contrast between the chemistry of the bis(dinitrogen) complexes of molybdenum and tungsten containing two bidentate tertiary phosphine ligands and those containing four monodentate tertiary phosphines is exemplified by two series of reactions.[4] First, reaction with strong protic acids leads to the formation of hydrazido(2−) complexes in the former series of bis(dinitrogen) complexes[5,6] (e.g., eq 1, where

$$trans\text{-}Mo(N_2)_2(dppe)_2 + 2HX \rightarrow MoX(NNH_2)(dppe)_2X + N_2 \quad (1)$$

dppe = $Ph_2PCH_2CH_2PPh_2$ and X = Br, I, or HSO_4) whereas in the latter series ammonia (and occasionally hydrazine) is produced (e.g., eq 2)[5c,7] The extent of this latter reaction (eq

$$cis\text{-}Mo(N_2)_2(PMe_2Ph)_4 \xrightarrow{HX} N_2 + NH_4X + HPMe_2PhX + Mo^{VI}? \quad (2)$$

2) is dependent on HX and the solvent used. Intermediates in the reaction have been isolated.[7,8]

Second, reaction of the $(dppe)_2Mo$ and -W complexes with alkyl bromides and iodides afford 2-alkyldiazenido-*N* derivatives[9,10] (e.g., eq 3, where R = Me, Et, etc. and X = Br or

$$Mo(N_2)_2(dppe)_2 + RX \rightarrow MoX(NNR)(dppe)_2 + N_2 \quad (3)$$

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