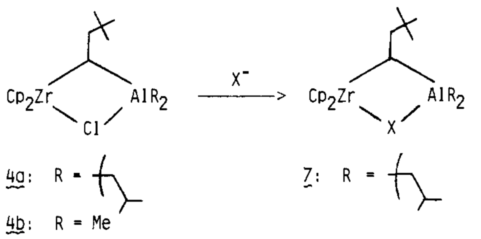
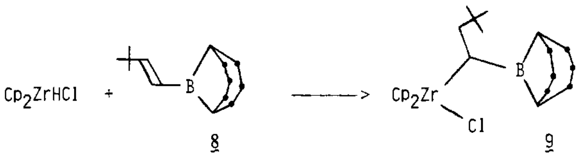
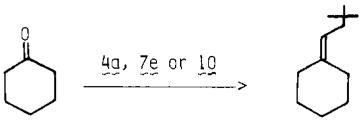
altered reactivity was the observation by proton NMR analysis that the more reactive the species, the further downfield were chemical shifts of the alkylidene protons. To prepare a series of analogues of **4**, therefore, was of interest for these zirconium species. Indeed, we find that addition of 1 equiv of either sodium methoxide, sodium thioethoxide, lithium diethylamide, lithium diphenylphosphide, or neopentyllithium to **4a** in benzene (followed by removal of the alkali metal chloride by filtration) gave a series of new complexes (reaction 4). The ^{1}H NMR spectra for **7a–e** (Table I) showed absorptions for the newly incorporated anionic ligands and, as well, a shift of the signal for the carbenoid proton, suggesting that **7a–e** are simple ligand metathesis analogues of the starting material. In the neopentyl complex (**7e**), the chemical shift of the α proton is comparable to that observed for the titanium–aluminum alkylidene complexes. As well, the chemical shift for the alkylidene carbon is shifted downfield to 191 ppm.



The mode of synthesis of the zirconium–aluminum compounds utilizing Cp_2ZrHCl is compatible with other alkenyl metal starting materials. For example, the addition of Cp_2ZrHCl to neohexenylborane **8**[17] gives a new complex **9** (reaction 5). [Its yellow color is typical of dicyclopentadienylalkylchlorozirconium species rather than the red bridging-alkylidene complexes.] The signal for the α proton appears in the ^{1}H NMR as a doublet of doublets centered at δ 3.16. Cp_2ZrHCl also adds to dineohexenylzinc[18] to give a bridging-alkylidene complex, **10**. Th α proton appears at δ 6.94 in the ^{1}H NMR spectrum.



Preliminary studies show that the alkylidene-bridged zirconium systems react with ketones to give "Wittig" products, although in low yield (20%). For example, both the aluminum species, **4a** and **7e**, and the zinc complex, **10**, convert cyclohexanone into neohexylidenecyclohexane[12] (reaction 6). We are currently exploring methods for activation of these readily prepared zirconium-based complexes with regard to their ultimate utilization as synthetic reagents. We are also examining means to improve titanium-based reagent systems.



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(17) Prepared by the addition of 9-borabicyclononane to 3,3-dimethyl-1-butyne.

(18) Prepared by the transmetalation reaction of dicyclopentadienylchloroneohexenylzirconium with $ZnCl_2$ in CH_2Cl_2.[15]

Bis(triphenylphosphine)iminium Nitrite. A Mild, Versatile Nitrosylating Reagent

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The majority of known metal clusters contain carbon monoxide as the predominant ligand, and with few exceptions, these clusters are sterically and electronically saturated. This fact, which certainly leads to their stability, unfortunately renders these clusters much less active as homogeneous catalysts under mild conditions. Thermolysis to achieve activation often results in disruption of the cluster since the metal–carbonyl bonds are stronger than the metal–metal bonds.[1] Substitution of an appropriate number of nitric oxide ligands for carbon monoxide is one possible method of bypassing this problem.

As part of our study of nitrosyl carbonyl clusters, we are exploring various synthetic methods for converting existing metal carbonyls into nitrosyl carbonyl compounds. The use of sodium nitrite as a nitrosylating reagent in the absence of acid has been restricted to only a few reactions.[2–6] The prototypal example, reported by Hieber and Beutner,[2] is the synthesis of $[Fe(CO)_3(NO)]^-$ (eq 1), which until now has been the only known nitrosyl carbonylmetalate.

$$\mathrm{Fe(CO)_5 + NaNO_2 + NaOCH_3 \xrightarrow[100\ ^{\circ}C]{CH_3OH,\ 1\ h} Na[Fe(CO)_3(NO)] + CO + Na(CH_3OCO_2)} \quad (1)$$

Recent attempts to extend this reaction to $Mo(CO)_6$ in order to form $[Mo(CO)_4(NO)]^-$ resulted instead in the incorporation of methoxide into the product forming $(PPN)_3[Na[Mo_3(CO)_6(NO)_3(\eta_2\text{-}OCH_3)_3(\eta_3\text{-}O)]_2]$.[5] To avoid such complications, we have prepared bis(triphenylphosphine)iminium nitrite ($PPNNO_2$) using the method of Martinsen and Songstad[7] and have discovered that in dipolar aprotic solvents it is indeed a mild and versatile nitrosylating reagent. This has allowed us to greatly improve the synthesis of three well-known nitrosyl carbonyl complexes and readily synthesize three new compounds including the second example of a nitrosyl carbonylmetalate.

When 1 equiv of $Fe(CO)_5$ is added to a dried and deoxygenated THF solution of $PPNNO_2$, rapid evolution of gas, identified as CO_2 and CO, is observed as the $PPNNO_2$ completely dissolves. After 10 min the solvent is removed from the bright yellow solution, yielding yellow crystals of $PPN[Fe(CO)_3(NO)]$ in virtually quantitative yield. This procedure can be contrasted with previous methods using $NaNO_2$ in hydroxylic solvents (eq 1) to produce the air-sensitive sodium salt $Na[Fe(CO)_3(NO)]$ followed by metathesis with PPNCl to give $PPN[Fe(CO)_3(NO)]$. The yield of this method, which requires approximately 2 days to complete, is 50%.[8]

The reactions of $PPNNO_2$ with cationic metal carbonyls are also rapid. One equivalent of $PPNNO_2$ reacts with $[Fe(CO)_2(PPh_3)_2(NO)](PF_6)$ at room temperature in acetonitrile to give the known dinitrosyl $Fe(CO)(PPh_3)(NO)_2$.[9] The reaction exhibits high selectivity in that none of the known $Fe(PPh_3)_2(NO)_2$ is observed, and considering the ease by which the starting cation

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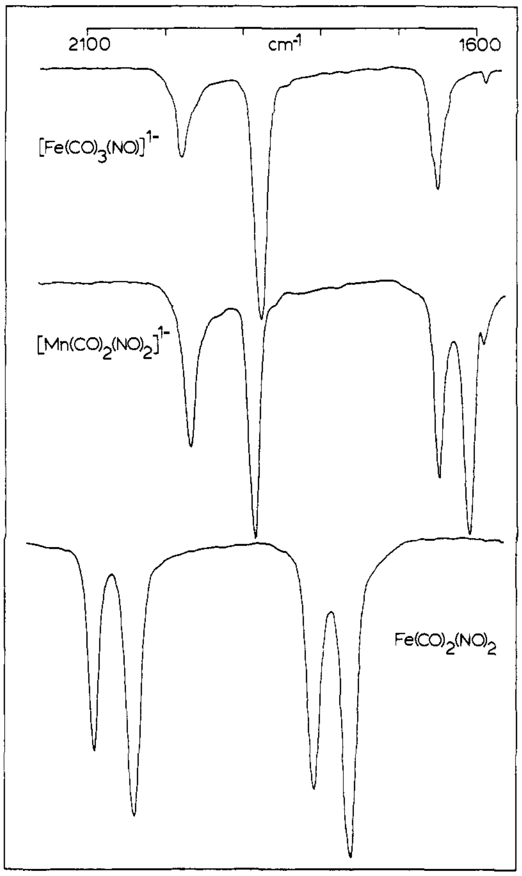
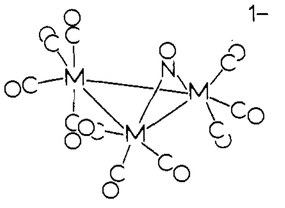


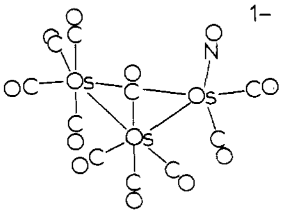
Figure 1. Infrared spectra of the ν_{CO} and ν_{NO} regions of PPN[Mn(CO)$_2$(NO)$_2$], PPN[Fe(CO)$_3$(NO)], and Fe(CO)$_2$(NO)$_2$ in THF. The small peak at 1590 cm^{-1} is due to the PPN cation.

is prepared,[10] it is the simplest method to synthesize Fe(CO)(PPh$_3$)(NO)$_2$. The hexacarbonyl cation of Mn also reacts with PPNNO$_2$. When 1 equiv of PPNNO$_2$ in acetonitrile is added to [Mn(CO)$_6$]BF$_4$ in acetonitrile at -40 °C, Mn(CO)$_4$NO is formed instantly. Addition of a second equivalent of PPNNO$_2$ to the reaction results in the formation of orange PPN[Mn(CO)$_2$(NO)$_2$][11] in high yield. This new, air-sensitive compound is only the second known example of a nitrosyl carbonylmetalate. It has been characterized by elemental analysis and its infrared spectrum, shown in Figure 1 along with a comparison with the spectra of PPN[Fe(CO)$_3$(NO)] and Fe(CO)$_2$(NO)$_2$. With the preparation of PPN[Mn(CO)$_2$(NO)$_2$], we can now begin to see the development of a series of isoelectronic nitrosyl carbonyl anions parallel to the neutral d^{10} series, which extends from Ni(CO)$_4$ to Cr(NO)$_4$. The d^{10} anionic series begins with [Co(CO)$_4$]$^-$ followed by [Fe(CO)$_3$(NO)]$^-$ and now includes [Mn(CO)$_2$(NO)$_2$]$^-$. The reactivity of these nitrosyl carbonylmetalates in various organic and organometallic systems is currently under investigation, and we have already reported that [Fe(CO)$_3$(NO)]$^-$ is itself useful reagent for preparing nitrosyl carbonyl clusters.[12]

Metal clusters readily react with PPNNO$_2$. When Ru$_3$(CO)$_{12}$ is combined with 1.5 equiv of PPNNO$_2$ in THF at room temperature, the new nitrosyl carbonyl cluster, PPN[Ru$_3$(CO)$_{10}$(NO)][13] is rapidly formed. After solvent removal under vacuum, the residue is triturated with hexane. The green powder is recrystallized from ether to give the product in 78% yield. Protonation of PPN[Ru$_3$(CO)$_{10}$(NO)] with CF$_3$COOH in CH$_2$Cl$_2$ produces Ru$_3$(CO)$_{10}$(NO)H which was originally prepared by Johnson and co-workers[14] by the reaction of [Ru$_3$(CO)$_{11}$H]$^-$ with NO$^+$. The reaction of PPNNO$_2$ with Os$_3$(CO)$_{12}$ is somewhat slower and requires 30 min at room temperature for completion. The ultimate product, which is the new cluster PPN[Os$_3$(CO)$_{10}$(NO)],[15] is obtained in 55% recrystallized yield. It can also be protonated to give the known species Os$_3$(CO)$_{10}$(NO)H.[14] The structures of the cluster anions, illustrated below (I), are likely very similar to their protonated analogues where the hydrogen was shown to bridge the same metal–metal bond as the nitrosyl ligand does. In the initial stage of the reaction of Os$_3$(CO)$_{12}$ with PPNNO$_2$, an intermediate is observed by infrared spectroscopy after 5 min which has an absorbance at 1621 cm^{-1}. This is attributed to a terminal nitrosyl bound to a negatively charged metal, possibly having the structure shown in II.

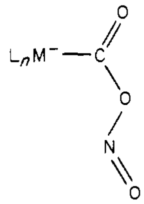


I (M=Ru or Os)



II

The greatly enhanced reactivity of NO$_2^-$ is apparently due to its increased nucleophilicity in the dipolar aprotic solvents. From the series of compounds studied, it appears that the first stage of this reaction involves nucleophilic attack of uncoordinated NO$_2^-$ on a coordinated carbon monoxide giving the intermediate III.



III

Although the order the precise nature of the remaining steps is undetermined, a reasonable mechanism might involve III undergoing a rearrangement which amounts to a migratory deinsertion of NO from carbon dioxide. This step is formally analogous to the decomposition of coordinated carboxylic acids[16] and requires the expulsion of a ligand such as CO from the metal. The final step would involve conversion of the bent NO to a linear NO with concomitant loss of CO$_2$. Further work to determine the mechanism should also help to evaluate the scope of the reaction.

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(13) IR of PPN[Ru$_3$(CO)$_{10}$(NO)] ν_{CO} (THF) 2067 w, 2035 m, 2010 vs, 2001 s, 1982 s, 1944 s; ν_{NO} not observed. Anal. Calcd: C, 47.96; H, 2.62; N, 2.43. Found: C, 47.73; H, 2.80; N, 2.38.

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(15) IR of PPN[Os$_3$(CO)$_{10}$(NO)] ν_{CO} (CH$_2$Cl$_2$) 2081 w, 2022 s, 2010 vs, 1988 s, 1947 m; ν_{NO} not observed. Anal. Calcd: C, 38.93; H, 2.13; N, 1.97. Found: C, 38.74; H, 2.17; N, 1.88.

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