Journal of Organometallic Chemistry, 347 (1988) 333–342
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Synthesis, characterization, and reactivity of PPN[$Cr(CO)_4(NO)$]

Daniel R. Mantell and Wayne L. Gladfelter *

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455 (U.S.A.)

(Received September 9th, 1987)

Abstract

The new nitrosyl carbonylmetalate PPN[$Cr(CO)_4(NO)$] has been synthesized from $Cr(CO)_6$ and PPN(NO_2) in THF (PPN = bis(triphenylphosphine)iminium cation). The material was characterized by infrared and ^{15}N NMR spectroscopy and by elemental analysis, which demonstrated it has the same structure as $Mn(CO)_4(NO)$. Kinetic experiments show the reaction to be first order in both chromium and nitrite with $k = 0.25 \pm 0.05\ M^{-1}\ sec^{-1}$ at $58.60 \pm 0.05\ °C$. A mechanism consistent with this and related results is discussed. Metal–carbon, metal–hydrogen, and metal–metal bonds have been formed by the reactions of PPN[$Cr(CO)_4(NO)$] with electrophiles ($CF_3SO_3CH_3$, CF_3SO_3H, Ph_3SnCl). With the labile complexes, $M(CO)_5(THF)$ (M = Cr, Mo and W), PPN[$Cr(CO)_4(NO)$] produces the homo- and hetero-dinuclear complexes PPN[$CrM(CO)_9(NO)$] (M = Cr, Mo and W).

Introduction

The attack of nucleophiles on the carbonyl carbon atoms of $Cr(CO)_6$ has been the subject of many synthetic and mechanistic studies [1]. The reaction of lithium and Grignard reagents with $Cr(CO)_6$ is the first step to the well-known Fisher-type carbenes [2]. Other anions such as hydroxide [3] and azide [4] have been shown to attack the carbon atoms, and even the neutral nucleophile, Me_3NO, attacks $Cr(CO)_6$ with a high second-order rate constant [5]. PPN(NO_2) has been found to be an effective nucleophilic nitrosylating reagent, eq. 1 [6,7].

$$M(CO)_n^x + PPN(NO_2) \rightarrow CO + CO_2 + [M(CO)_{n-2}(NO)]^{x-1} \qquad (1)$$

Although related reactions of $Mo(CO)_6$ and $W(CO)_6$ with nitrite in the presence of methoxide (which is incorporated into the product) have been reported [8], no studies of the chromium analog have appeared. In this paper we discuss the study of the reaction of PPN(NO_2) with $Cr(CO)_6$. The mechanism of formation of PPN[$Cr(CO)_4(NO)$] is described along with a survey of its reactivity as a nucleophile.

0022-328X/88/$03.50

Experimental

PPN(Cl) [9], PPN(NO_2) [10], and M$(CO)_5$(THF) (M = Cr, Mo, and W) [11] were prepared according to published procedures. M$(CO)_6$ (M = Cr, Mo and W), Ph_3SnCl, and Cr$(acac)_3$ were purchased and used without further purification. CF_3SO_3H and $CF_3SO_3CH_3$ were distilled under reduced pressure prior to use. Tetrahydrofuran (THF) and diethyl ether were dried by distillation from sodium benzophenone ketyl under N_2. Hexane was dried by distillation from Na under N_2, and methylene chloride was dried by distillation from P_2O_5 under reduced pressure directly into the reaction vessel. All reactions were conducted under an atmosphere of N_2 using standard Schlenk techniques. Chromatography was conducted on silica gel using hexane as the eluent. Infrared spectra were obtained on a Beckman 4250 infrared spectrophotometer or a Mattson Cygnus 25 FTIR equipped with a HgCdTe detector. ^{15}N and ^{1}H NMR were obtained on a Nicolet NT CFT-1180 300 MHz or a Varian HFT-80 spectrometer. The samples for ^{15}N NMR experiments were prepared from $Na^{15}NO_2$ (90% enriched, Merck, Sharp and Dohme). Spectra were taken in CH_2Cl_2 (3.0 ml) in a 12 mm tube with a sample concentration of 0.003 *M* and with 0.03 *M* Cr$(acac)_3$ added as a shiftless relaxation reagent. External referencing utilized CH_3NO_2 in $CHCl_3$ with 0.03 *M* Cr$(acac)_3$ set at 379.60 ppm downfield from NH_3 (liquid, 25 ° C) [12]. Electron impact mass spectra were obtained on a AEI MS-30 mass spectrometer at 70 eV. Elemental analyses were performed by Galbraith Laboratories Inc. A summary of the spectroscopic data is included in Table 1.

Preparation of PPN[Cr(CO)$_4$(NO)]. PPN(NO_2) (268 mg, 0.458 mmol) and Cr$(CO)_6$ (100 mg, 0.454 mmol) were placed in a Schlenk tube. THF (20 ml) was added via syringe through a septum and the slurry was stirred at 55 ° C for 4 h. The

Table 1

Spectroscopic data

Compound	Color	ν(CO) (cm^{-1})	ν(NO) (cm^{-1}) (^{15}NO)	$\delta(^{15}N)$ (ppm)	$\delta(^{1}H)$ (ppm)
PPN[Cr$(CO)_4$(NO)]	red	1993m, 1895vs, 1850vs (THF)	1608s (1577s)	448.5 (CH_2Cl_2)	
$Ph_3SnCr(CO)_4(NO)$	yellow	2088w, 2029m, 2015vs (hexane)	1750 (1715s)	406.9 (CH_2Cl_2)	7.5 (CD_2Cl_2)
$CH_3Cr(CO)_4(NO)$	yellow	2032vs, 1991m (THF)	1735m (1690m)	384.9 (CH_2Cl_2)	−0.72 (CD_2Cl_2)
$HCr(CO)_4(NO)$	yellow	2029vs, 1978w (THF)	1740m		−4.85 (CD_2Cl_2)
PPN[$Cr_2(CO)_9$(NO)]	orange	2058w, 1950vs, 1893vs, 1870m (THF)	1675s (1642s)	401.8 (CH_2Cl_2)	
PPN[CrMo$(CO)_9$(NO)]	orange	2060w, 1990m, 1940vs, 1901m, 1870s(THF)	1670vs (1635vs)	404.8 (CH_2Cl_2)	
PPN[CrW$(CO)_9$(NO)]	orange	2061w, 1995m, 1943vs, 1900vs, 1875s (THF)	1678vs (1645vs)	403.3 (CH_2Cl_2)	
PPN[Cr$(CO)_5$(NO_2)]	yellow	1927s, 1876m (THF)		530.9 (CH_2Cl_2)	

solution turned from colorless to a deep wine red. The reaction was monitored by infrared spectroscopy which showed a smooth decline of the carbonyl stretch due to $Cr(CO)_6$ while absorptions due to $[Cr(CO)_4(NO)]^-$ (see Table 1) grew in. After cooling to room temperature, the volume was reduced under vacuum to approximately 5 ml and filtered to remove a small amount of tan solid. A red brown crystalline solid was precipitated by addition of ether (40 ml). The material was isolated by filtration and washed with ether (2 × 10 ml), giving $PPN[Cr(CO)_4(NO)]$ (306 mg, 0.417 mmol) in 92% yield. Anal. Found: C, 65.41; H, 4.30; N, 3.70. $CrP_2O_5N_2C_{40}H_{30}$ calcd.: C, 65.58; H, 4.13; N, 3.82%.

Preparation of $Ph_3SnCr(CO)_4(NO)$. $PPN[Cr(CO)_4(NO)]$ (100 mg, 0.136 mmol) was dissolved in THF (2 ml). To this solution was added Ph_3SnCl (158 mg, 0.536 mmol), causing the color to change from red to yellow and a white solid to precipitate from solution. The mixture was filtered, the solvent was removed under vacuum, and the remaining yellow solid was extracted into hexane. Excess Ph_3SnCl was removed by chromatography. $Ph_3SnCr(CO)_4(NO)$ eluted first as a yellow band followed by a colorless band of Ph_3SnCl. Evaporation of the hexane gave $Ph_3SnCr(CO)_4(NO)$ as a yellow crystalline solid (51 mg, 0.094 mmol, 69% yield). $Ph_3SnCr(CO)_4(NO)$ is an air stable material which can be stored in air for months with no decomposition. Anal. Found: C, 48.86; H, 3.07; N, 2.69. $CrSnO_5NC_{22}H_{15}$ calcd.: C, 48.57; H, 2.78; N, 2.58%. Mass spectrum: *m/e* 544, $[Ph_3SnCr(CO)_4(NO)]^+$; 467, $[Ph_2SnCr(CO)_4(NO)]^+$; 402, $[Ph_3SnCr]^+$; 350, $[Ph_3Sn]^+$; 273, $[Ph_2Sn]^+$.

Reaction of $PPN[Cr(CO)_4(NO)]$ with $CF_3SO_3CH_3$. $PPN[Cr(CO)_4(NO)]$ (54 mg, 0.074 mmol) was dissolved in CH_2Cl_2 (8 ml) at −30 °C. $CF_3SO_3CH_3$ (8.3 μl, 0.073 mmol) was added via syringe and stirred at −30 °C for 0.5 h. The color changed from the deep wine red of $PPN[Cr(CO)_4(NO)]$ to a light red. The ^1H NMR and infrared spectrum showed changes consistent with the formation of $CH_3Cr(CO)_4(NO)$. The reaction was warmed to room temperature over the period of 0.5 h causing a color change to yellow and then to brown. Removal of the solvent under reduced pressure gave a brown solid. Extraction with hexane, in which it apparently has greater stability, gave only enough material to see the most intense absorptions of $CH_3Cr(CO)_4(NO)$ along with some $Cr(CO)_6$.

Reaction of $PPN[Cr(CO)_4(NO)]$ with CF_3SO_3H. $PPN[Cr(CO)_4(NO)]$ (43 mg, 0.059 mmol) was dissolved in CH_2Cl_2 (5 ml) at −78 °C. CF_3SO_3H (7.8 μl, 0.088 mmol) was added via syringe causing the color lighten. The reaction was warmed to −30 °C causing a color change to yellow. The ^1H NMR and infrared spectrum showed changes consistent with the formation of $HCr(CO)_4(NO)$. Attempts to remove solvent resulted in decomposition to an insoluble brown material.

Preparation of $PPN[Cr_2(CO)_9(NO)]$. $PPN[Cr(CO)_4(NO)]$ (122 mg, 0.167 mmol) was dissolved in THF (5 ml) and transferred via cannula to a solution of $Cr(CO)_5(THF)$ (prepared from 35 mg (0.159 mmol) of $Cr(CO)_6$ in THF (15 ml)). Unreacted $PPN[Cr(CO)_4(NO)]$ was precipitated by the addition of ether (40 ml) and removed by filtration. The solvent was removed under vacuum and the orange residue extracted with ether (30 ml). Hexane was added until the solution turned cloudy. Bright orange crystals of $PPN[Cr_2(CO)_9(NO)]$ were precipitated by slow removal of ether under reduced pressure. The product was isolated by filtration (63 mg, 0.068 mmol, 43% yield). Anal. Found: C, 58.77; H, 3.58; N, 2.80. $Cr_2P_2O_{10}N_2C_{45}H_{30}$ calcd.: C, 58.45; H, 3.27; N, 3.03%.

Preparation of PPN[CrMo(CO)$_9$(NO)]. The same procedure as above was followed using PPN[Cr(CO)$_4$(NO)] (125 mg, 0.171 mmol) and Mo(CO)$_5$(THF) [prepared from 55mg (0.208 mmol) of Mo(CO)$_6$] giving bright orange crystals of PPN[CrMo(CO)$_9$(NO)] (85 mg, 0.088 mmol, 51% yield). Anal. Found: C, 55.70; H, 3.41; N, 2.69. $CrMoP_2O_{10}N_2C_{45}H_{30}$ calcd.: C, 55.80; H, 3.12; N, 2.89%.

Preparation of PPN[CrW(CO)$_9$(NO)]. The same procedure as above was followed using PPN[Cr(CO)$_4$(NO)] (200 mg, 0.273 mmol) and W(CO)$_5$(THF) (prepared from 200 mg (0.568 mmol) of W(CO)$_6$) giving bright orange crystals of PPN[CrW(CO)$_9$(NO)] (205 mg, 0.194 mmol, 71% yield). Anal. Found: C, 50.86; H, 2.99; N, 2.61. $CrWP_2O_{10}N_2C_{45}H_{30}$ calcd.: C, 51.16; H, 2.86; N, 2.65%.

Preparation of PPN[Cr(NO$_2$)(CO)$_5$]. Cr(CO)$_5$(THF) was prepared as above using Cr(CO)$_6$ (58 mg, 0.264 mmol). This solution was added to a slurry of PPN(NO$_2$) (154 mg, 0.263 mmol) in THF (5 ml) at 0 ° C. The volume was reduced to approximately 5 ml and filtered. A yellow crystalline material was precipitated from solution by the addition of ether (40 ml) and isolated by filtration (113 mg, 0.145 mmol, 55% yield). PPN[Cr(NO$_2$)(CO)$_5$] is an air sensitive and thermally unstable material which darkens over a period of days when stored under N_2 at room temperature. Anal. Found: C, 62.66; H, 4.86; N, 3.48. $CrP_2O_7N_2C_{41}H_{30}$ calcd.: C, 63.40; H, 3.89; N, 3.61%.

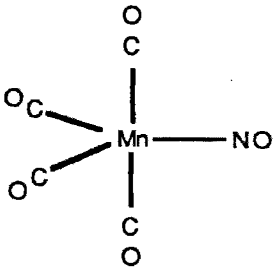
Thermolysis of PPN[Cr(NO$_2$)(CO)$_5$]. PPN[Cr(NO$_2$)(CO)$_5$] (20 mg, 0.026 mmol) was dissolved in THF (5 ml) and heated to 55 ° C. The infrared spectrum showed only decline of absorbances due to starting material. No new absorptions in the carbonyl or nitrosyl regions were observed over a period of 5 h.

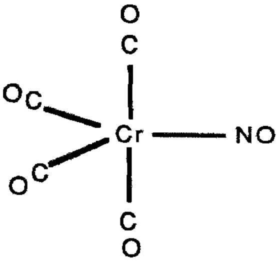
Kinetic analysis of the reaction of PPN(NO$_2$) with Cr(CO)$_6$. THF solutions of known concentrations (approximately 1.0 m*M*) of PPN(NO$_2$) were prepared in volumetric flasks under N_2. Measured volumes of the PPN(NO$_2$) solutions were transferred to a N_2-filled Schlenk tube containing a known amount of Cr(CO)$_6$ (enough for approximately 1 m*M*). Rapid mixing insured immediate dissolution of the Cr(CO)$_6$. The temperature of the reactions were maintained at 58.60 ± 0.05 ° C. Aliquots were withdrawn over periods lasting from 1.5 to 3 h, placed in a N_2-flushed NaCl infrared cell and the transmittances at 1850 cm^{-1} measured. The concentration of $[Cr(CO)_4(NO)]^{1-}$ was determined from a calibration curve of concentration vs. percent transmittance. Data were measured over a range of 1.5 to just under 3 half-lives. An average $k = 0.25 \pm 0.05$ M^{-1} sec^{-1} was determined.

Results and discussion

Reaction of NO_2^- with Cr(CO)$_6$. PPN(NO$_2$) reacts with Cr(CO)$_6$ in THF over a period of 4 h to form the new nitrosyl carbonylmetalate, PPN[Cr(CO)$_4$(NO)], in nearly quantitative yield. The other products of the reaction are CO and CO_2. Monitoring the reaction by infrared spectroscopy revealed smooth decline of the CO stretch due to Cr(CO)$_6$ as the intensity of the absorptions due to $[Cr(CO)_4(NO)]^-$ increased; no intermediates were observed. PPN[Cr(CO)$_4$(NO)] is obtained as a red brown crystalline material by addition of ether to THF solutions. It is air sensitive, but in the crystalline state it can be manipulated in air over short periods of time with little decomposition. Slow decomposition is observed over a period of weeks even when stored at −20 ° C under an atmosphere of purified N_2. The unidentified gray decomposition material is easily removed by recrystallization. PPN[Cr(CO)$_4$-

(NO)] has been characterized by infrared and ^{15}N NMR spectroscopy, elemental analysis, and its chemical reactivity. The infrared spectrum is very similar to that of its isoelectronic neutral analog, $Mn(CO)_4(NO)$ [13]. Infrared absorptions of the chromium compound show an approximate 120 cm^{-1} shift to lower energy in the carbonyl stretching region. The nitrosyl stretch is also shifted to lower energy by approximately 150 cm^{-1}. These shifts are consistent with the negative charge on the chromium complex. The above similarities suggest that $PPN[Cr(CO)_4(NO)]$ has a structure analogous to that of $Mn(CO)_4(NO)$, which has been determined at low temperature by single crystal X-ray analysis [14]. $PPN[Cr(CO)_4(^{15}NO)]$ has a ^{15}N chemical shift of 448.5 ppm which falls in the linear nitrosyl range [7,15–18].





Characterization of $PPN[Cr(NO_2)(CO)_5]$. $PPN(NO_2)$ reacts with $Cr(CO)_5(THF)$ displacing the THF and giving a yellow crystalline material proposed to be $PPN[Cr(NO_2)(CO)_5]$. The carbonyl stretching region of the infrared spectrum is very similar to that of $PPN[CrI(CO)_5]$ and other $[CrX(CO)_5]^-$ salts [19]. Although the elemental analysis is slightly off (0.74% for C and 0.97% for H), when combined with the spectroscopic data, a reasonable case for the formulation as $PPN[Cr(NO_2)(CO)_5]$ can be made.

Infrared spectroscopy is one useful method for distinguishing between the two possible linkage isomers of nitrite [20]. Nitro (N-bound) complexes have a $\nu_a(NO_2)$ in the region of 1470 and 1370 cm^{-1} and a $\nu_s(NO)_2$ from 1340 to 1320 cm^{-1}, while O-bound (nitrito) ligands give rise to bands in the ranges from 1485 and 1400 cm^{-1} and 1110 to 1050 cm^{-1}. Samples of $PPN[Cr(NO_2)(CO)_5]$, $PPN[Cr(^{15}NO_2)(CO)_5]$, and PPN(Cl) were separately deposited on a NaCl plate from THF or CH_2Cl_2 solution by evaporation under N_2. The samples were examined by FTIR spectroscopy, and the difference spectrum in the region of interest is shown in Fig. 1. One large band (perhaps composed of two separate absorptions) attributed to the nitro ligand is observed from 1323 to 1303 cm^{-1} (1280 to 1260 cm^{-1} for $^{15}NO_2{}^-$). While this is in the correct region for the $\nu_s(NO_2)$, the antisymmetric stretch (if it is contributing to this band) is 50 cm^{-1} below its normal range. The compounds used to establish the above stated range were Werner-type complexes of metals in higher oxidation states. The lowering of the $\nu_a(NO_2)$ may be a result of increased π-backbonding from the d^6 Cr to the nitro ligand.

In the spectrum of the ^{15}N enriched compound a weak peak that is not completely due to PPN^+ is observed at 1379 cm^{-1}. Unfortunately, no analogous peak was found in the ^{14}N species, however, the expected region is obscured by a strong PPN^+ absorption. Normally, the intensities of the two nitro peaks are similar to each other, which reduces the probability that the 1379 cm^{-1} peak is due to the $\nu_a(^{15}NO_2)$. Because of the smaller quantity of enriched compound being manipulated, it is possible that this absorption is due to an impurity. Finally, we emphasize

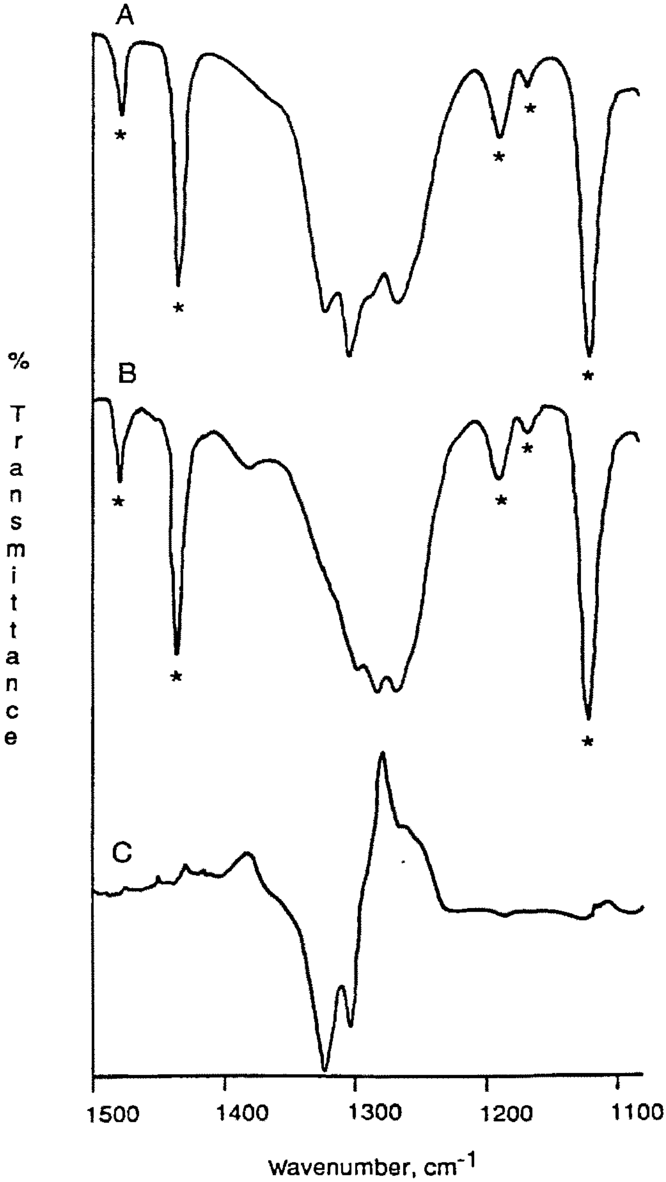
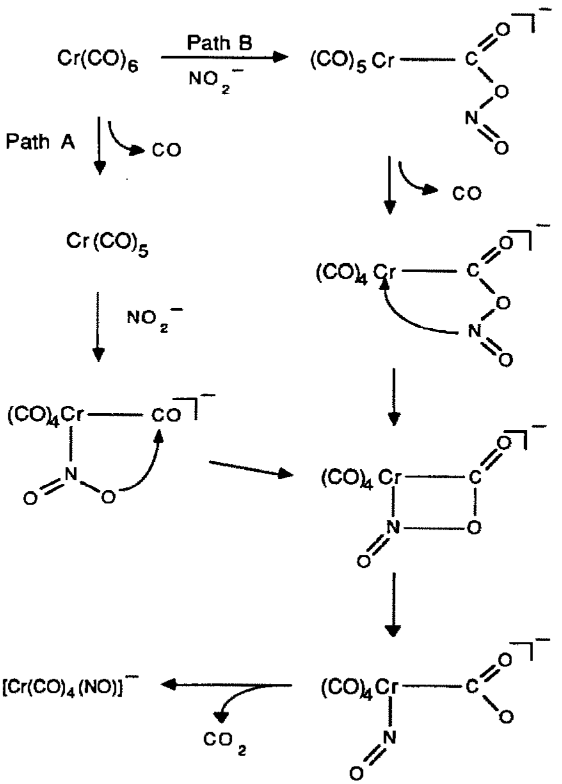


Fig. 1. Comparison of the infrared spectra in the nitro and nitrito regions of PPN[Cr(NO_2)(CO)$_5$] (A), PPN[Cr($^{15}NO_2$)(CO)$_5$] (B) (deposited on NaCl plates), and the difference (C = A − B) between them after substracting the absorptions due to PPN(Cl). The asterisks indicate absorptions entirely due to PPN^+.

that no absorptions are observed in (or near) the lower energy region characteristic of a nitrito ligand.

^{15}N NMR spectroscopy should be very sensitive to the different environments of a nitrito vs. nitro ligand because of the presence or absence of an uncoordinated lone pair of electrons on the nitrogen. This was found to be true for the organic analogs: $\delta(^{15}N)$ for n-butyl nitrite is 572 ppm while $\delta(^{15}N)$ for nitrobenzene is 372 ppm [12]. Unfortunately, few measurements of $\delta(^{15}N)$ of nitro complex of transition



Scheme 1

metals have been made, and none for nitrito ligands have been reported. The $\delta(^{15}N)$ for the nitro ligand of *trans*-$[Rh(Cl)(NO_2)(PPh_3)_2]$ appears at 425 ppm [16]. $PPN[Cr(^{15}NO_2)(CO)_5]$ has one resonance in the ^{15}N NMR at 530.9 ppm, which places it in between the nitro and anticipated (based on organonitrites) nitrito regions, but closer to the latter. While these two spectroscopic studies give conflicting views of the linkage isomer present, we favor the nitro isomer as suggested by the IR spectrum. In this case ^{15}N NMR spectroscopy is less helpful due to the absence of good models for evaluating the chemical shift of a nitrito ligand, and $\delta(^{15}N)$ of nitrogenous ligands is very sensitive to changes of the metal complex.

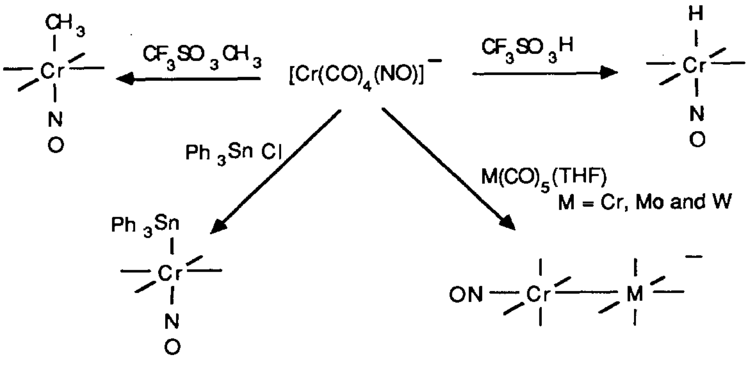
Mechanism of reaction of nitrite with $Cr(CO)_6$. Two reaction mechanisms for the formation of $PPN[Cr(CO)_4(NO)]$ seem plausible (Scheme 1). Path A involves the dissociation of CO to from the unsaturated (or solvent stabilized) species $Cr(CO)_5$ which can add nitrite. Loss of CO_2 after oxygen atom transfer to a carbonyl carbon would give the observed product. Such oxygen atom transfer form nitro ligands to CO are not uncommon and have been mechanistically studied [21–24]. Path B is similar to one proposed for the reaction of $PPN(NO_2)$ with $Fe(CO)_5$ in acetonitrile [6]. An initial attack by nitrite on a carbonyl carbon would form an acylnitrite intermediate. The next step would involve loss of CO and migration of the nitrogen to the metal center. Loss of CO_2 would give the observed product.

Kinetic experiments establish that the reaction is first order in both reactants and not inhibited by CO. These results are not consistent with path A. Further evidence against path A was obtained by the actual synthesis and subsequent pyrolysis of the proposed intermediate PPN[$Cr(NO_2)(CO)_5$]. The material did not give the observed nitrosyl product when placed under identical reaction conditions and, in fact, only decomposed.

At 58.6 °C the specific rate constant in THF for the formation of PPN[$Cr(CO)_4(NO)$] is 0.25 ± 0.05 M^{-1} sec^{-1}. The analogous reaction of PPN(NO_2) with $Fe(CO)_5$ in acetonitrile at 26 °C is 0.111 M^{-1} sec^{-1} [6]. Qualitatively, we have found that reactions of nitrite with metal carbonyls are slightly faster in THF. Thus, under identical solvent and temperature conditions the rate of the $Cr(CO)_6$ and NO_2^- would be slower than the reaction of $Fe(CO)_5$ with NO_2^-.

It is interesting to compare the reactivity of nitrite to other nucleophiles that are known to attack carbonyl carbons of $Cr(CO)_6$. The rate of azide (as the Et_4N^+ salt) reaction with $Cr(CO)_6$ at 50 °C in acetone was reported to be 0.0685 M^{-1} sec^{-1} [25]. These conditions are quite similar to those used in the current study, and a comparison of the results suggests that nitrite is a slightly better nucleophile towards the carbonyl carbon of $Cr(CO)_6$ than azide. Not surprisingly, organometallic nucleophiles such as benzyl magnesium bromide [26] and methyl lithium [27] are much more reactive, whereas halides (which are also proposed to attack the carbonyl carbon) are much less reactive [28,29]. Recent reports on the high reactivity of the oxygen atom donor Me_3NO, which has a rate nearly the same as that found for the Grignard reagent, establish it to be much more reactive than nitrite [5].

Reactivity of PPN[Cr(CO)$_4$(NO)]. As with other carbonylmetalates and nitrosyl carbonylmetalates, $[Cr(CO)_4NO]^-$ acts as a nucleophile towards a variety of reagents (Scheme 2). The reaction of PPN[$Cr(CO)_4(NO)$] with Ph_3SnCl produces PPN(Cl) and $Ph_3SnCr(CO)_4(NO)$, however, more than one equivalent of Ph_3SnCl is required to drive the reaction to completion. The unreacted Ph_3SnCl is removed by chromatography, and $Ph_3SnCr(CO)_4(NO)$ is obtained as an air stable yellow crystalline material. Absorptions in the infrared spectrum are shifted to higher energy by approximately 140 cm^{-1} when compared to the starting anion. The pattern of the infrared spectrum is similar to those of the second and third row transition metal analogs of $Ph_3SnCr(CO)_4(NO)$ which were prepared by Graham and coworkers from the reaction of $[Ph_3SnM(CO)_5]^-$ with NO^+ (M = Mo and W)



Scheme 2. Reactions of $[Cr(CO)_4(NO)]^-$.

[30]. The Cr analog, however, could not be prepared by this route. The Mo and W compounds were shown to have the nitrosyl ligand *trans* to the Ph_3Sn ligand, and it is proposed that $Ph_3SnCr(CO)_4(NO)$ has the same C_{4v} structure as its Mo and W analogs. The ^{15}N NMR spectrum has a single resonance at 406.0 ppm.

The reaction of PPN[$Cr(CO)_4(NO)$] with CF_3SO_3R ($R = CH_3$ and H) proceeds at low temperature to give what is proposed to be the alkylated and protonated species. The yellow solutions of the two compounds were characterized by infrared and by ^1H and ^{15}N (for $R = CH_3$) NMR spectroscopy. The expected shift to higher energy was observed for the carbonyl and nitrosyl stretching regions of the infrared spectrum. Comparison to the isoelectronic analogs, $RMn(CO)_5$ ($R = CH_3$ and H) show that both compounds gave ^1H NMR resonances in the expected regions (chemical shift (ppm): $CH_3Mn(CO)_5$, 0.28 [31]; $CH_3Cr(CO)_4(NO)$, -0.72; $HMn(CO)_5$, -7.73 [32]; $HCr(CO)_4(NO)$, -4.85). Neither compound was isolated due to decomposition upon warming or removal of solvent. The instability of both $HCr(CO)_4(NO)$ and $CH_3Cr(CO)_4(NO)$ seems to be similar to the analogous products formed from $[Fe(CO)_3(NO)]^-$. $HFe(CO)_3(NO)$ decomposes above $-45\,^\circ C$ [33], and the only alkylated product obtained from the methylation of $[Fe(CO)_3(NO)]^-$ was an acyl, $Fe(CO)_2(PPh_3)(NO)[C(O)CH_3]$, which required the addition of phosphine to the methylation reaction itself [34]. $CH_3Cr(CO)_4(^{15}NO)$ has one resonance in the ^{15}N NMR spectrum at 384.9 ppm.

In the reaction of PPN[$Cr(CO)_4(NO)$] with $M(CO)_5(THF)$ (M = Cr, Mo and W) the THF ligand is easily displaced and a new metal–metal bond is formed. The products can be isolated as bright orange crystalline material from ether/hexane solutions by slow evaporation of the ether under reduced pressure. Absorptions in the infrared spectrum of the products exhibit a shift to higher energy relative to $[Cr(CO)_4(NO)]^-$, roughly half the shift found in the neutral products discussed above. Each of the three compounds has a single resonance in the linear nitrosyl region of the ^{15}N NMR spectrum (Table 1). Single crystal diffraction studies have been performed on a protonated ditungsten analog of the dinuclear species discussed above [35]. Neutron scattering data showed that the nitrosyl ligand of $HW_2(CO)_9(NO)$ was located exclusively in the axial position, and that the hydride was bridging the metals.

Although specific rate comparisons were not made, the nucleophilicity of $[Cr(CO)_4(NO)]^-$ seems to be less than that found for $[Mn(CO)_5]^-$. This observation is consistent with the concept that the nitrosyl ligand is a better π-accepting ligand than the carbonyl group.

Acknowledgement

This research was supported by a grant from the National Science Foundation.

References

1 S.W. Kirtley, in G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, New York, 1982; Vol. 3, 799–800.

2 D.J. Cardin, B. Cetinkaya, M.F. Lappert, Chem. Rev., 72 (1972) 545.

3 M.D. Grillone, B.B. Kedzia, J. Organomet. Chem., 140 (1977) 161.

4 W. Beck, H. Werner, H. Engelmann, H.S. Smedal, Chem. Ber., 101 (1968) 2143.

5 Y.L. Shi, Y.C. Gao, Q.Z. Shi, D.C. Kershner, F. Basolo, Organometallics, 6 (1987) 1528.

6 R.E. Stevens, W.L. Gladfelter, Inorg. Chem., 22 (1983) 2034.
7 W.L. Gladfelter, Adv. Organomet. Chem., 24 (1985) 41.
8 S.W. Kirtley, J.P. Chanton, R.A. Loue, D.L. Tipton, T.N. Sorrell, R. Bau, J. Am. Chem. Soc., 102 (1980) 3451.
9 J.K. Ruff, W.S. Schlienty, Inorg. Syn., 15 (1974) 84.
10 A. Martinsen, J. Songstad, Acta Chem. Scand., Ser. A, 31 (1977) 645.
11 W. Strohmeier, Angew. Chem., Int. Ed. Eng., 3 (1969) 730.
12 G.C. Levy, R.L. Lichter, Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy, Wiley, New York, 1979.
13 P.M. Treichel, E. Pitcher, R.B. King, F.G.A. Stone, J. Am. Chem. Soc., 83 (1961) 2593.
14 B.A. Frenz, J.H. Enemark, J.A. Ibers, Inorg. Chem., 8 (1969) 1288.
15 R.E. Botto, B.W.S. Kolthammer, P. Legzdins, J.D. Roberts, Inorg. Chem., 18 (1979) 2049.
16 L.K. Bell, J. Mason, D.M.P. Mingos, D.G. Tew, Inorg. Chem., 22 (1983) 3497.
17 D.H. Evans, D.M.P. Mingos, J. Mason, A. Richards, J. Organomet. Chem., 249 (1983) 293.
18 J. Mason, Chem. Britain, (1983) 654.
19 E.W. Abel, I.S. Butler, J.G. Reid, J. Chem. Soc., (1963) 2068.
20 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Organometallic Compounds, 3rd ed., Wiley, New York, 1978.
21 D.T. Doughty, G. Gordon, R.P. Stewart, Jr., J. Am. Chem. Soc., 101 (1979) 2645.
22 R.D. Feltham, J.C. Kriege, J. Am. Chem. Soc., 101 (1979) 5064.
23 R.D. Doughty, R.P. Stewart, Jr., G. Gordon, J. Am. Chem. Soc., 103 (1981) 3388.
24 J. Kriege-Simondsen, G. Elbaze, M. Dartiguenave, F.R. Feltham, Y. Dartiguenave, Inorg.Chem., 21 (1982) 230.
25 H. Werner, W. Beck, H. Engelmann, Inorg. Chim. Acta, 3 (1969) 331.
26 M.Y. Darensbourg, H.L. Conder, D.J. Darensbourg, C. Hasday, J. Am. Chem. Soc., 95 (1973) 5919.
27 G.R. Dobson, J.R. Paxson, J. Am. Chem. Soc., 95 (1973) 5925.
28 J.E. Pardue, M.N. Memering, D.R. Dobson, J. Organomet. Chem., 71 (1974) 407.
29 K.J. Asali, G.R. Dobson, J. Organomet. Chem., 179 (1979) 169.
30 E.E. Isaacs, W.A.G. Graham, J. Organomet. Chem., 99 (1975) 119.
31 R.B. King, Organomet. Synth., 1 (1965) 147.
32 G.M. Whitesides, G. Maglio, J. Am. Chem. Soc., 91 (1969) 4980.
33 W. Hieber, H.Z. Beutner, Anorg. Allg. Chem., 320 (1963) 101.
34 K.H. Pannell, Y. Chen, K. Belknap, C. Wu, I. Bernal, M.W. Creswick, N.H. Huang, Inorg. Chem., 22 (1983) 418.
35 J.P. Olsen, T.F. Koetzle, S.W. Kirtley, M.A. Andrew, D.L. Tipton, R. Bau, J. Am. Chem. Soc., 96 (1974) 6621.