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Preliminary communication

A CONVENIENT ROUTE TO NEW CYCLOPENTADIENYLDINITROSYLTUNGSTEN COMPOUNDS

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Summary

$[C_5H_5W(NO)_2CO]PF_6$ has been prepared and shown to be a useful precursor for a variety of new cationic and neutral tungsten nitrosyl compounds.

The cyclopentadienyldinitrosylcarbonyl cation of chromium, $[C_5H_5Cr(NO)_2CO]^+$, has been known for some time [1] and together with $[C_5H_5Mn(CO)_2NO]^+$ [2] and $[C_5H_5Fe(CO)_3]^+$ [3] forms a long-recognized isoelectronic series. Although second or third row analogs of the manganese and iron cations, e.g. $[C_5H_5Re(CO)_2NO]^+$ [4] and $[C_5H_5Ru(CO)_3]^+$ [5], have since been prepared, such is not the case for chromium. In recent years much attention has been given to reactions of the manganese [6,7], rhenium [8], iron [9—11], and ruthenium [12] cations with various nucleophilic reagents. We report here the high-yield synthesis of the $[C_5H_5W(NO)_2CO]^+$ cation, the first higher analog of $[C_5H_5Cr(NO)_2CO]^+$, and the results of some preliminary studies involving its reactivity towards several neutral and anionic nucleophiles.

The reaction of nitrosyl hexafluorophosphate ($NOPF_6$) with $C_5H_5W(CO)_2NO$ in dichloromethane/acetonitrile at —78° afforded $[C_5H_5W(NO)_2CO]PF_6$ (I) as a green solid in ~90% yield. (Anal.: Found: C, 15.09; H, 1.18; N, 5.84. Calcd.: C, 14.95; H, 1.05; N, 5.81%.) The infrared spectrum (Nujol) showed one carbonyl stretching band at 2116 cm^{-1} in addition to two nitrosyl stretching bands at 1814 and 1730 cm^{-1}. These band positions are substantially lower than the corresponding frequencies (Nujol) in the chromium analog $[C_5H_5Cr(NO)_2CO]PF_6$ [1] (ν(CO) 2137 cm^{-1}, ν(NO) 1873, 1779 cm^{-1}), perhaps reflecting a greater degree of backbonding in the case of the third row metal atom. It is noteworthy that a similar trend in ν(CO) and ν(NO) is observed when one compares $[C_5H_5Mn(CO)_2NO]^+$ vs. $[C_5H_5Re(CO)_2NO]^+$ [4] and $C_5H_5Cr(CO)_2NO$ vs. $C_5H_5W(CO)_2NO$ [13].

The compound is insoluble in non-polar solvents, ether, and dichloromethane. The addition of coordinating solvents such as acetonitrile or acetone to solid I is accompanied by vigorous gas evolution and formation of reactive dark green solutions containing the $[C_5H_5W(NO)_2S]^+$ cations ($S = CH_3CN$, $(CH_3)_2CO$). In the former case the same species was formed when $C_5H_5W(CO)_2NO$ was allowed to react with $NOPF_6$ in acetonitrile at room temperature. The extreme lability of the carbonyl group in I is in marked contrast to the behavior of $[C_5H_5Cr(NO)_2CO]PF_6$ which can be recrystallized from acetone solutions [1].

As a result of its very labile carbonyl group $[C_5H_5W(NO)_2CO]PF_6$ offers a convenient synthetic route to a variety of cationic and neutral nitrosyl derivatives. This is illustrated by the nucleophilic substitution reactions shown in Eqn. 1:

$$[C_5H_5W(NO)_2CO]PF_6 \begin{cases} \xrightarrow[CH_2Cl_2]{L} [C_5H_5W(NO)_2L]PF_6 \\ \\ \xrightarrow[(CH_3)_2CO]{NaX} C_5H_5W(NO)_2X \end{cases} \tag{1}$$

$L = PPh_3$, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$; $X = Cl$, Br, I

Thus a slurry of I in dichloromethane reacted rapidly under reflux with various neutral Lewis bases (L) to form the corresponding substituted compounds $[C_5H_5W(NO)_2L]PF_6$ * ($L = PPh_3$, $AsPh_3$, $SbPh_3$, $P(OMe)_3$, $P(OPh)_3$] in good yield (62—82%). These green crystalline solids are insoluble in non-polar solvents and ether but are readily soluble in dichloromethane and acetone. Nitrosyl stretching frequencies for these compounds are shown in Table 1 and appear to correlate with the σ-donor/π-acceptor properties of the L groups. Similar substitution reactions involving $[C_5H_5Cr(NO)_2CO]PF_6$ have not been reported**, although such reactions have been studied in some detail for the related $[C_5H_5Mn(CO)_2NO]^+$ cation [7].

TABLE 1

INFRARED SPECTRA

Compound	$\nu(NO)$ (cm^{-1}) [a]	
$[C_5H_5W(NO)_2PPh_3]PF_6$	1770	1696
$[C_5H_5W(NO)_2AsPh_3]PF_6$	1771	1697
$[C_5H_5W(NO)_2SbPh_3]PF_6$	1770	1697
$[C_5H_5W(NO)_2P(OMe)_3]PF_6$	1777	1702
$[C_5H_5W(NO)_2P(OPh)_3]PF_6$	1788	1712
$C_5H_5W(NO)_2Cl$	1735	1651
$C_5H_5W(NO)_2Br$	1737	1654
$C_5H_5W(NO)_2I$	1740	1657

[a] CH_2Cl_2 solution

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*Satisfactory elemental analyses (C, H, N) and proton NMR spectra have been obtained for these compounds.

**The $[C_5H_5Cr(NO)_2PPh_3]^+$ cation has been briefly mentioned [14].

Addition of solid I to NaX (X = Cl, Br, I) in acetone solution at room temperature resulted in vigorous gas evolution and formation of the neutral olive-green to green crystalline compounds $C_5H_5W(NO)_2X$[*] (yield 56—75%). Appropriate infrared data are listed in Table 1. The qualitative air stability of these compounds (in both the solid state and in solution) appears to decrease in the order X = I > Br > Cl. The mass spectra of these halides exhibited the molecular ion and peaks due to $C_5H_5W(NO)X^+$, $C_5H_5WX^+$, $C_3H_3WX^+$, and $C_3H_3W^+$ in moderate to high abundance.

In spite of the fact that the analogous chromium compounds were initially prepared in 1956 [15], until now the only known molybdenum or tungsten derivative of this type was the rather unstable $C_5H_5Mo(NO)_2Cl$ [16][**]. The synthetic method employed here is similar to that used to prepare the related $C_5H_5M(CO)_2X$ derivatives from the corresponding $[C_5H_5M(CO)_3]^+$ cations (M = Fe, Ru) [18].

We are currently investigating further reactions of $[C_5H_5W(NO)_2CO]$-PF_6 with other nucleophilic reagents (e.g., BH_4^-, LiR, RMgX) and the synthetic utility of the derivatives reported here. Parallel studies involving molybdenum are also in progress in these laboratories.

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[*] Satisfactory elemental analyses (C, H, N) and proton NMR spectra have been obtained for these compounds.

[**] Related tri-1-pyrazolylborate complexes of the type $RB(pz)_3M(NO)_2Cl$ have been reported (M = Mo, W) [17].