Journal of Organometallic Chemistry, 94 (1975) 61—64

PREPARATION OF THE GROUP VI PENTACARBONYL NITRATES*

JOHN L. CIHONSKI and ROBERT A. LEVENSON*
Department of Chemistry, Texas A&M University, College Station, Texas 77843 (U.S.A.)
(Received February 10th, 1975)

Summary

Pentacarbonyl nitrate anions of Cr and W have been prepared by reaction of tetraethylammonium nitrate with the photochemically generated $M(CO)_5THF$ intermediates.

The manganese [1] and rhenium [2,3] pentacarbonyl nitrates, $M(CO)_5NO_3$, have been prepared by the reaction of excess liquid dinitrogen tetroxide with the respective decacarbonyl. $Mn(CO)_5NO_3$ has also been prepared by an even more complex synthetic route [4]. Addition of N_2O_4 to $M(CO)_6$ (M = Cr, Mo, W) in an attempt to prepare the Group VI nitrates resulted in the loss of all carbonyl groups [2,3]. No attempts have been reported using N_2O_4 and the $M_2(CO)_{10}^{2-}$ ions [5]**. An alternative approach to $M(CO)_5NO_3^-$ is prompted by the work of Strohmeier [6] who irradiated THF solutions of the appropriate $M(CO)_6$ in the presence of ligands L to prepare numerous $M(CO)_5L$ complexes. The suggested mechanism is shown in reactions 1 and 2 where L is any ligand which is a better electron donor than THF. L may also be added after irradiation because the $M(CO)_5THF$ intermediate is stable in a nitrogen atmosphere [7]. Thus, since the addition of L is done at room temperature and not during irradiation, the possibility of complicated side reactions is greatly reduced.

$$M(CO)_6 + THF \xrightarrow{h\nu} M(CO)_5THF + CO \qquad (1)$$

$$M(CO)_5THF + L \longrightarrow M(CO)_5L + THF \qquad (2)$$

We herein report the preparation of the complex anions $M(CO)_5NO_3^-$ (M = Cr, W). Vibrational spectra are reported and assigned by comparison with the Group VI and VII halide and the Group VII nitrate analogues. Ultraviolet-visible spectra data are also reported

---

[*] This research constitutes partial fulfillment of the Ph.D. requirements of J.L.C.
[**] We have recently learned that the $M(CO)_5NO_3^-$ species can be prepared by the reaction of the $M_2(CO)_{10}^{2-}$ anions with $AgNO_3$ [5a].

Experimental

The hexacarbonyls and tetraethylammonium nitrate were commercially obtained and used without further purification. All solvents were freshly purified and purged with nitrogen prior to use. Infrared spectra were obtained with a Beckman IR-12 spectrometer. The Raman spectrum was obtained with a Cary 81 Raman spectrophotometer using the 647.1 nm line of a CRL 52B krypton ion laser. Ultraviolet-visible spectra were recorded on a Cary-14 spectrophotometer.

Preparation of $Et_4N[W(CO)_5NO_3]$. A 20 ml THF solution of 0.3 g $W(CO)_6$ is irradiated under nitrogen as previously described [7]. An equal molar amount of $(Et_4N)NO_3$ in 20 ml CH_2Cl_2 is added to the $W(CO)_5THF$ intermediate after irradiation is terminated. From this point the work-up should be carried out as rapidly as possible. Petroleum ether (30-60°C) is added to the solution until the first sign of a precipitate is apparent. The solution is filtered and additional petroleum ether added to the filtrate to produce a yellow crystalline precipitate ($\approx$0.13 g; 30% yield). The product may be recrystallized from THF—petroleum ether. It must be dried by allowing it to stand in a nitrogen atmosphere since vacuum pumping leads to decomposition. (Analysis found: C, 30.76; H, 3.28; N, 5.20. $C_{13}H_{20}N_2O_8W$ calcd.: C, 30.23; H, 3.87; N, 5.40%.) The yellow chromium complex was prepared in a similar manner; the stability of this compound did not permit its being sent for commercial analysis. The molybdenum analog could not be isolated as a solid.

Discussion

The stability of the products in solution increases from chromium to tungsten. An alcoholic solution of $W(CO)_5NO_3^-$ exposed to oxygen is relatively stable at room temperature compared to a similar solution of the chromium complex which shows signs of rapid decomposition; under these conditions approximately 20% of the tungsten complex decomposed in 0.5 h. The parent hexacarbonyl is observed to be one of the decomposition products for both compounds, presumably according to the scheme discussed by Darensbourg and Brown [8]. They are less stable thermally than their Group VII analogues [1-4]. In the solid state both compounds are considerably more stable than in solution but the chromium complex shows signs of discoloration after several days at room temperature. The compounds may be stored at —5°C under nitrogen for several weeks without signs of decomposition. The complexes are photochemically inactive as judged by the fact that irradiation of $W(CO)_5NO_3^-$ in CH_2Cl_2 in the presence of PPh_3 (for 0.5 h) resulted in no new bands in the infrared spectrum; under the same conditions $W(CO)_6$ and $W(CO)_5$-PPh_3 both undergo reaction [9].

Vibrational data are presented in Table 1. Solution Raman spectra could not be obtained because of low stability in solution, particularly during laser irradiation. The chromium analogue decomposed at very low laser power (<15 milliwatts) even in the solid state and thus it was not possible to obtain a spectrum. For the tungsten complex only the carbonyl region could be observed in the Raman since the lower energy (and less intense) vibrations could not be

TABLE 1

SPECTROSCOPIC DATA FOR THE GROUP VI PENTACARBONYL NITRATES

$Et_4N[Cr(CO)_5NO_3]$ IR (cm^{-1})[a]	$Et_4N[W(CO)_5NO_3]$ IR (cm^{-1})[a]	Raman (cm^{-1})[b]	Assignment
2058w	2068w	2070m	A_1^{eq}
		1985s	B_1
1930s	1936s		E
1874m	1887m	1857m	A_1^{ax}
1385s	1405s		
1306s	1296s		
1125m	1020s		
807m	794s		
653s	602s		
439s	436w		
364w	361s		

[a] In $CHCl_3$ for ν(CO) region; KBr pellet otherwise. [b] Solid state.

observed at a laser power that would not decompose the compound. The spectra are similar in intensity and position to that of the the Group VI carbonyl halides [10] and the same assignments are made. However, unlike the case of $Re(CO)_5NO_3$ [3] we observe no splitting of the E vibration. In both complexes a band ca. 1983 cm^{-1} was present which increased in intensity with time. This band, which can be attributed to the parent hexacarbonyls [11], is also at the same frequency as the B_1 mode. This was verified by the Raman spectrum of $W(CO)_5NO_3^-$ in which a band at 1985 cm^{-1} is the strongest in the spectrum; this is consistent with data for $Re(CO)_5NO_3$ [3]. The carbonyl frequencies are shifted to lower energy relative to the Group VII analogues by ca. 100 cm^{-1}, in agreement with the expected trend upon change in oxidation state of the central metal atom [12]. Because of the lack of sufficient data, no specific assignments have been made for the remaining bands; assignments for $Re(CO)_5NO_3$ [3] were greatly facilitated by the ability to obtain the Raman spectrum.

In recording the ultraviolet-visible spectrum of the chromium derivative extinction coefficients were not obtained because of the relatively rapid decomposition; band maxima in EtOH are at 429.4 and 226.7 nm. For $W(CO)_5NO_3^-$, transitions are seen at 468.1(498), 416.8(3100), 336.2(915), 301.7(1620), 286.4(3140), 245.7(4900), and 217.6(26,900) nm (ϵ values in parentheses). The energies and number of peaks are in agreement with the electronic spectra of the Group VI halide analogues [13,14]. The spectra of the Group VI $M(CO)_5$pyridine complexes [15] (which have the same overall symmetry as the nitrato complexes) show a splitting of the first band in the Cr complex when compared to the halides complexes; the same is true for the 416.8 nm band in the W analogue (the first band is presumably spin forbidden). Such a splitting, presumably of a d–d transition to an excited E state in C_{4v} symmetry, is not observed for $M(CO)_5NO_3^-$. This difference may be caused by the ability of pyridine to act as a π-acceptor, while nitrate is expected to be a π-donor. Since low-valent transition metal complexes function much more readily as π-acceptors, the pyridine—metal interaction should be more effective than the nitrate—metal interaction in lifting the degeneracy of the d_{xz} and d_{yz} orbitals. Indeed, Fenske has suggested that no significant π-interaction exists between the potentially π donor halides X and the metal in $M(CO)_5X^-$ type complexes [16].

Acknowledgement

This research was supported by the Robert A. Welch Foundation (Grant A-509).

References

1 C.C. Addison, M. Kilner and A. Wojcicki, J. Chem. Soc., (1961) 4839.
2 C.C. Addison, R. Davis and N. Logan, Inorg. Chem., 6 (1967) 1926.
3 C.C. Addison, R. Davis and N. Logan, J. Chem. Soc. A, (1970) 3333.
4 M.L.H. Green and P.L.J. Nagy, Advan. Organometal. Chem., 2 (1964) 325.
5 L.B. Handy, J.K. Ruff and L.F. Dahl, J. Amer. Chem. Soc., 92 (1970).
5a J.K. Ruff, private communication.
6 W. Strohmeier, Angew. Chem. Int. Ed. Engl., 3 (1964) 730.
7 J.K. Ruff, Inorg. Chem., 8 (1969) 86.
8 D.J. Darensbourg and T.L. Brown, Inorg. Chem., 7 (1968) 1679.
9 G. Schwenzer, M.Y. Darensbourg, and D.J. Darensbourg, Inorg. Chem., 11 (1972) 1967.
10 E.W. Abel, I.S. Butler and J.G. Reid, J. Chem. Soc., (1963) 2068.
11 F.A. Cotton and C.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 4432.
12 E.W. Abel, Quart. Rev., 17 (1963) 137.
13 R.A.N. McLean, J. Chem. Soc. Dalton, (1974) 1568.
14 M. Wrighton, Inorg. Chem., 13 (1974) 905.
15 P.H. Pettit, Jr., Ph.D. Thesis, Lehigh University (1969).
16 R.F. Fenske and R.L. DeKock, Inorg. Chem., 9 (1970) 1053.