9,9′-10,10′ bisanthracenic photocyclomers V linked by a poly(oxyethylene) chain.[4c,19] In contrast, in the complex I,2Na$^+$ the interaction of the oxygen lone pairs with the cation may be expected to decrease the repulsion experienced in the free ligand and, in so doing, to restore the normal regioselectivity of the photoprocess. This aspect was examined by irradiation of a NaClO$_4$-saturated methanolic solution of I, under the same conditions as above, and although no photoproduct was isolated, evidence for the formation of essentially the photocyclomer 9,9′-10,10′ III,2Na$^+$ is obtained from the following observations: (i) the anthracenic ^1L_a band (310–420 nm) disappeared without any significant growing in of a naphthalenic absorption, (ii) the disappearance quantum yield of I was at least 1 order of magnitude greater ($\phi_R > 4 \times 10^{-3}$) than that observed from the cation free solution, and (iii) in the dark, the photoproduct underwent an almost quantitative fast thermal back reaction with a rate ($k_{\text{diss}} \simeq 7 \times 10^{-4}$ s^{-1}) close to that recorded for compounds V;[19] this last feature can be explained by a competition between MeOH and I to solvate Na$^+$; the desolvated photocyclomer III then is thermally unstable and reverts to the anthracenophane I.

A greater understanding of such systems in which fluorescence and photochemistry can be cation directed and an improvement of their physical properties are under current investigation.

Acknowledgment. We thank Dr. M. Lamotte for recording the fluorescence spectra of the crystalline samples and J. Lauret for the synthesis of the starting materials. We are much obliged to Dr. A. Gilbert, visiting professor, for his assistance in preparation of the manuscript.

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Insertion of the Nitrosonium Ion into a Chromium-Methyl Bond[1,2]

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Insertion reactions of metal–carbon σ bonds are an integral and important part of transition-metal organometallic chemistry.[3] Of these reactions, the conversions involving the thermodynamically spontaneous migratory insertion of coordinated nitric oxide, i.e.,[4]

$$\text{ON—M—R} \rightarrow \text{M—N(=O)—R} \xrightarrow{\text{L}} \text{L—M—N(=O)—R} \quad (1)$$

(where R = alkyl and L = Lewis base) are of particular interest since they lead to the formation of new carbon–nitrogen bonds.

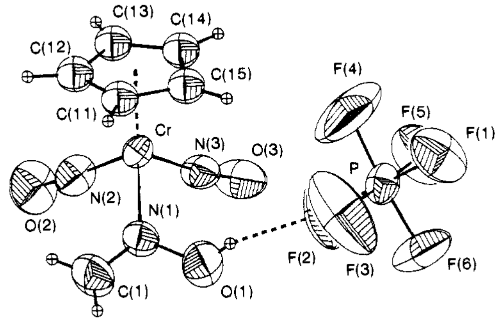

Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$. Selected bond lengths (Å) and angles (deg): C(1)–N(1) = 1.253 (9), N(1)–O(1) = 1.392 (7), Cr–N(1) = 2.034 (5), Cr–N(2) = 1.702 (6), Cr–N(3) = 1.709 (5), N(2)–O(2) = 1.163 (6), N(3)–O(3) = 1.152 (6), Cr–C$_5$H$_5$(centroid) = 1.843, H(10)–F(2) = 2.14 (8), Cr–N(1)–C(1) = 128.9 (5), C(1)–N(1)–O(1) = 111.5 (6), O(1)–N(1)–Cr = 119.6 (4), N(2)–Cr–N(3) = 93.5 (3), O(2)–N(2)–Cr = 174.5 (6), O(3)–N(3)–Cr = 172.2 (5).

We now wish to report the first instance of the formation of a C–N linkage by the insertion of NO$^+$ into a transition-metal–carbon bond. Specifically, we present the conditions for effecting the transformation

$$(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3 + NOPF_6 \xrightarrow{CH_2Cl_2} [(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6 \quad (2)$$

and describe in detail the characterization of the novel product, a rare organometallic formaldoxime complex.

In a typical experiment, a green solution of $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$[5] (0.384 g, 2.00 mmol) in CH$_2$Cl$_2$ (20 mL) was treated with solid NOPF$_6$ (0.280 g, 1.60 mmol), and the mixture was stirred at room temperature under N$_2$. After 1 h, a dark green, microcrystalline solid began to precipitate. This solid was collected by filtration after 3.5 h and was recrystallized from CH$_2$Cl$_2$ to obtain 0.260 g (44% yield based on NOPF$_6$) of analytically pure[6] $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$ as green, diamagnetic crystals. The crystals are moderately air-stable and are most soluble in solvents such as nitromethane.[7]

A single-crystal X-ray crystallographic analysis of the formaldoxime complex[8] established the cation as a normal "three-legged piano stool" (Figure 1). Within the cation, the $(\eta^5\text{-}C_5H_5)Cr(NO)_2$ fragment closely resembles that found in $(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl$.[9] Furthermore, the H$_2$CN(OH)Cr portion is essentially planar, and the intramolecular dimensions of the formaldoxime ligand resemble

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(1) Organometallic Nitrosyl Chemistry. 28. For part 27, see: Hunter, A. D.; Legzdins, P. *Organometallics*, in press.

(2) Taken in part from: Wassink, B. Ph.D. Dissertation, The University of British Columbia, Vancouver, Canada, 1985.

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(5) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.

(6) Anal. Calcd for C$_6$H$_8$N$_3$O$_3$PF$_6$Cr: C, 19.63; H, 2.20; N, 11.45. Found: C, 19.39; H, 2.15; N, 11.11. IR (Nujol mull) ν_{NO} 1854 (s), 1761 (s), 996 (m) cm^{-1}, 3480 (m), 1646 (w) cm^{-1}; IR (CH$_2$Cl$_2$) ν_{NO} 1847 (m), 1746 (m) cm^{-1}; IR (CH$_3$NO$_2$) ν_{NO} 1847 (s), 1748 (s) cm^{-1}; ^{1}H NMR (CD$_3$NO$_2$) δ 8.84 (d, 1 H, $^4J_{^1H_A-H_X}$ = 0.9 Hz, H_XONCH$_A$H$_B$), 7.67 (d, 1 H, $^2J_{^1H_A-^1H_B}$ = 5.1 Hz, H$_X$ONCH$_A$$H_B$), 7.30 (dd, 1 H, H$_XONCH_AH_B$), 6.08 (s, 5 H, C$_5$$H_5$); ^{1}H NMR (CD$_2Cl_2$) δ 8.92 (s, br, 1 H, H_XONCH$_A$H$_B$), 7.66 (d, 1 H, $^2J_{^1H_A-^1H_B}$ = 5.2 Hz, H$_X$ONCH$_A$$H_B$), 7.14 (d, 1 H, H$_XONCH_AH_B$), 5.98 (s, 5 H, C$_5$$H_5$); ^{13}C{^{1}H} NMR (CD$_3NO_2$) δ 159.1 (s, HONCH$_2$), 105.4 (s, C_5H$_5$); ^{13}C NMR (gated ^{1}H decoupled) (CD$_3$NO$_2$) δ 159.0 (dd, $^1J_{^{13}C-^1H}$ = 178.7, 186.9 Hz, HONCH$_A$H$_B$), 105.3 (dm, $^1J_{^{13}C-^1H}$ = 183.1 Hz, C_5H$_5$).

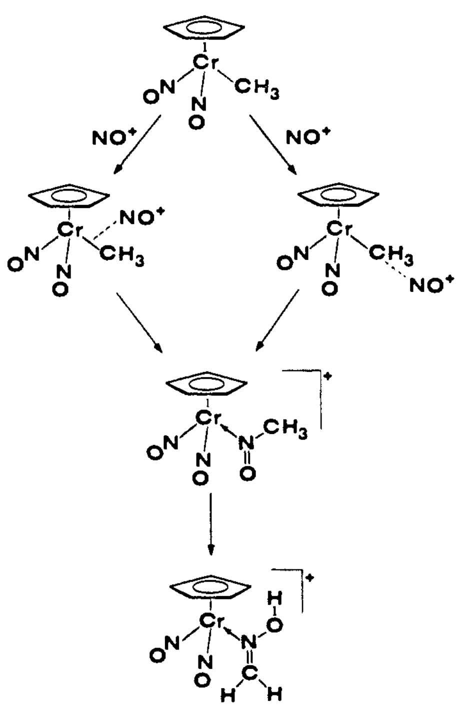
(7) Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261.

(8) X-ray diffraction data for $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$: monoclinic; space group $P2_1/c$; a = 7.903 (3) Å, b = 12.192 (2) Å, c = 13.417 (5) Å; β = 95.59 (2)°; V = 1286.6 Å^3; Z = 4; absorption coefficient = 10.71 cm^{-1}; diffractometer, Enraf-Nonius CAD4F; radiation, Mo Kα, graphite monochromator ($\lambda(K\alpha_1)$ = 0.709 30 Å); scan range = $0° \leqslant 2\theta \leqslant 50°$; reflections = 1262 with $I_0 \geqslant 3\sigma I_0$; R = 0.045, R_w = 0.050; error in observation of unit weight = 1.79e. All atoms except for the cyclopentadienyl H atoms were refined. Disorder involving two orientations of both the C$_5$H$_5$ ring and the F atoms of the anion equatorial with respect to the oxime OH group was accommodated during refinement (Watkins, D. J.; Carruthers, F. R. "CRYSTALS"; Chemical Crystallography Laboratory; University of Oxford, England, 1984). Only one orientation of the C$_5$H$_5$ ring is depicted in Figure 1, and F atoms having occupancy factors <0.5 are omitted.

(9) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795.

0002-7863/86/1508-0317$01.50/0

Scheme I



those of free formaldoxime.[10] In valence-bond terms, the bonding within this grouping is thus best represented as

$$\mathrm{Cr} \leftarrow \mathrm{N({=}CH_2)OH}$$

with the ligand functioning as a formal two-electron donor. The hydroxyl H atom of the formaldoxime ligand is also linked by a hydrogen bond [H(10)-F(2) = 2.14 (8) Å] to the counteranion.[11] The spectroscopic properties of $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$[6] can be readily understood in terms of its solid-state molecular structure, thus indicating that the basic structural units persist in solutions.

The two most likely mechanistic pathways for the unprecedented reaction 2 are those involving either oxidatively induced, intramolecular insertion of bound NO into the Cr-CH_3 bond[13] or charge-controlled, intermolecular attacks by NO^+ at the Cr-CH_3 group. At present, we favor the latter pathways (Scheme I)[15] since oxidation of $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ by $[Fe(phen)_3]^{3+}$ followed by treatment with NO does not afford the formaldoxime product of reaction 2.[18] It thus appears that reaction 2 occurs because $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ is relatively difficult to oxidize and its Cr-CH_3 bond is prone to nonoxidative attack by electrophiles.[19] Experiments designed to determine the scope of this new synthetic route to C-N bonds and to confirm the mechanism of reaction 2 are currently in progress.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and F.W.B.E. and a graduate scholarship to B.W.

Supplementary Material Available: Tables of fractional coordinates and isotropic and anisotropic thermal parameters for $[(\eta^5\text{-}C_5H_5)Cr(NO)_2\{N(CH_2)OH\}]PF_6$ (4 pages). Ordering information is given on any current masthead page.

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[10] Levine, I. N. *J. Chem. Phys.* **1963**, *38*, 128.

[11] A similar feature has been observed for $[(\eta^5\text{-}C_5H_5)_3Mn_3(\mu_2\text{-}NO)_3(\mu_3\text{-}NOH)]PF_6$.[12]

[12] Legzdins, P.; Nurse, C. R.; Rettig, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 3727.

[13] Related oxidatively promoted alkyl to acyl migratory insertions have been documented.[14]

[14] Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 5790 and references therein.

[15] In this scheme, the attack by NO^+ is portrayed as being a classical S_E2 process.[16] Also, the isomerization of the CH_3NO ligand to bound $CH_2{=}NOH$ shown in the last step is probably facilitated by the acidic species present, an inference that has ample literature precedents.[17]

[16] Rogers, W. N.; Page, J. A.; Baird, M. C. *Inorg. Chem.* **1981**, *20*, 3521 and references therein.

[17] Boyer, J. H. In "The Chemistry of the Nitro and Nitroso Groups"; Feuer, H., Ed.; Wiley-Interscience: Toronto, 1969; Part 1.

[18] At room temperature in CH_2Cl_2, $(\eta^5\text{-}C_5H_5)Cr(NO)_2CH_3$ (ν_{NO} 1777 (s), 1669 (s) cm^{-1}) is completely converted by 1 equiv of $[Fe(phen)_3]^{3+}$ into a $(\eta^5\text{-}C_5H_5)Cr(NO)_2^+$-containing product[2] ($\nu_{NO}$ 1846 (s), 1745 (s) cm^{-1}).

[19] Legzdins, P.; Wassink, B., unpublished observations.

Substrate and Positional Selectivity of the Gas-Phase Nitration of Substituted Benzenes by Protonated Methyl Nitrate. The First Example of a Well-Behaved Aromatic Nitration by a Gaseous Cation

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The central role played by electrophilic nitration in the theory of aromatic substitution[1] has stimulated mass spectrometric approaches to its study in the gas phase. Unfortunately, the available results delineate reactivity patterns dominated by processes, e.g., charge exchange and oxygen-atom transfer, peculiar of mass spectrometric conditions and hardly consistent with solution-chemistry data. Thus, NO_2^+ fails to add to arenes, and the other reagents used, $CH_2ONO_2^+$ and $EtO(NO_2)_2^+$, nitrate *deactivated* substrates at *higher* rates.[2-4] Futhermore, the lack of discrimination between isomeric nitrated adducts has prevented so far the crucial evaluation of positional selectivity.

We report a gas-phase ionic nitration whose substrate and positional selectivity, measured with a combination of mass spectrometric and radiolytic techniques, conform to common experience in condensed-phase nitration. The electrophile used, $MeO^+(H)NO_2$, belongs to a class of nitrating reagents well-known in solution[6] and is readily obtained in the gas phase, e.g., it represents a major ion in the CH_4 chemical ionization (CI) spectrum of methyl nitrate, arising from the exothermic[7] process

$$C_nH_5^+ + MeNO_3 \rightarrow C_nH_4 + MeO^+(H)NO_2 \qquad n=1,2 \qquad (1)$$

According to MINDO calculations,[8] the protonated ester in its most stable structure (H_f° = 150.5 kcal mol^{-1}) can be regarded as a nitronium ion "solvated" by methanol, with a binding energy of ca. 34 kcal mol^{-1}. The CI spectra of $CH_4/MeNO_3/C_6H_6$ mixtures display an abundant[9] nitrated adduct, of unknown structure, arising from the process

$$C_6H_6 + MeO^+(H)NO_2 \rightarrow C_6H_6NO_2^+ + MeOH \qquad (2)$$

Replacement of C_6H_6 with C_6D_6 yields comparable amounts of $C_6D_6NO_2^+$ and $C_6D_5HNO_2^+$. Analogous adducts are formed from

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[1] Cf.: Schofield, K. "Aromatic Nitration"; Cambridge Press: London, 1980.

[2] Benezra, S. A.; Hoffman, M. K.; Bursey, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7501-7502.

[3] Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 967-969.

[4] Ausloos, P.; Lias, S. G. *Int. J. Chem. Kinet.* **1978**, *10*, 657-667.

[5] Dunbar, R. C.; Shen, J.; Olah, G. A. *J. Am. Chem. Soc.* **1972**, 6862-6864.

[6] Raudnitz, H. *Chem. Ber.* **1927**, *69*, 738-743. See also ref 1, p 94, and references therein.

[7] Calculations based on the heat of formation of $MeO^+(H)NO_2$ given in ref 8 and on data from Cox and Aue [(a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 2-53] lead to ΔH° values of −57 and −22 kcal mol^{-1} for the proton transfer from CH_5^+ and $C_2H_5^+$, respectively.

[8] Dewar, M. J. S.; Shanshal, M.; Worley, S. D. *J. Am. Chem. Soc.* **1969**, *91*, 3590-3594.

[9] The CI spectra were recorded at CH_4 pressures up to ca. 0.5 torr and a source temperature of 150 °C, using a Hewlett-Packard 5982A quadrupole spectrometer or a ZAB-2F magnetic instrument (Micromass Ltd.). The ionic abundance of the $C_6H_6NO_2^+$ adduct in the CI spectra of $CH_4/MeNO_3/C_6H_6$ mixtures (molar ratios 1:0.016:0.002) ranges from 16% at ca. 0.25 torr to 26% at ca. 0.5 torr.

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