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Formation of Coordinated *C*-Nitroso Compounds by Reaction of K[$IrCl_5NO$] with Alkenes

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Summary: Coordinated C-nitrosochloroalkanes were obtained by electrophilic addition of K[$IrCl_5NO$] to cyclooctene or dicyclopentadiene; in the last case, the crystal structure of trans-[$IrCl_4(CH_3CN)$(syn-1-chloro-2-nitroso-1,2-dihydrodicyclopentadiene)] was determined by X-ray diffraction. Although the reaction between NOCl and alkenes is well-known, there are very few examples of clean electrophilic addition of coordinated NO^+ to alkenes.

C-Nitroso compounds are interesting not only due to their intrinsic chemical properties but also because of the discovery of their important role in a variety of metabolic processes.[1,2] As Gowenlock and Richter-Addo have recently stated,[3] the relatively high reactivity of these compounds imposes restrictions on the methods employed for their preparation. If they are obtained by oxidation of some precursor, the desired product may be oxidized to the nitro derivative, and isomerization to the corresponding oxime ($R_2C(H)NO \leftrightarrows R_2C{=}NOH$) can restrict the selection of the solvent for the preparation of primary and secondary nitrosoalkanes. However, a wide variety of synthetic routes exist for the preparation of these compounds with high yields, and in the last two decades these techniques have been improved or new ones have been developed.

Reactions of olefins with different electrophiles have been extensively studied. In particular, the product of the addition reaction of nitrosyl chloride to dicyclopentadiene was described to yield the dimeric nitroso chloride, which was converted to the blue monomer by dissolving it in hot solvents.[4] It has also been well established that nitrosyl chloride adds to norbornene and norbornadiene without rearrangement.[5] The infrared stretching frequency for the NO moiety of the product from norbornadiene was determined (1572 cm^{-1}), and it was shown that the product of addition was only the syn-exo unrearranged isomer.[6]

On the other hand, only a few reactions between coordinated nitrosyl and carbanions—yielding the *C*-nitroso compound—have been described, involving the following: nitroprusside and sp^3 carbanions (enolates from simple ketones, acetophenones, and derivatives from malonic acid),[7] ruthenium nitrosyls and acetone,[8] aromatic secondary and tertiary amines (leading the *p*-nitrosoarene complexes),[9] and just one reaction between a ruthenium nitrosyl and an alkyne.[10] None of them involve an alkene as the nucleophile, and only in a few cases could the product be crystallized. There are a few examples of reactions of Co−NO complexes with alkenes, which produce cobalt dinitrosoalkanes.[11]

In this work we describe the preparation of coordinated nitrosoalkanes from a nitrosyl complex and alkenes and their characterization. Only a few examples of *C*-nitrosoalkane complexes have been previously crystallized, all of them containing an ethyl, *tert*-butyl, or isopropyl radical.[12]

The nitrosyl in K[$IrCl_5NO$], according to its extremely high IR frequency[13] and its electrochemical behavior,[14] is probably

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(1) (a) Filehne, W. *Arch. Exptl. Pathol. Pharmakol.* **1878**, *9*, 329−379. (b) Loeb, R. F.; Bock, A. V.; Fitz, R. *Am. J. Med. Sci.* **1921**, *161*, 539−546.

(2) (a) Schenkman, J. B.; Wilson, B. J.; Cinti, D. L. *Biochem. Pharmacol.* **1972**, *21*, 2373−2383. (b) Franklin, M. R. *Mol. Pharmacol.* **1974**, *10*, 975−985. (c) Mansuy, D.; Beaune, P.; Cresteil, T.; Bacot, C.; Chottard, J.-C.; Gans, P. *Eur. J. Biochem.* **1978**, *86*, 573−579. (d) Lee, J.; Chen, L.; West, A. H.; Richter-Addo, G. B. *Chem. Rev.* **2002**, *102*, 1019−1065.

(3) Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Rev.* **2004**, *104*, 3315−3340.

(4) (a) Kraemer, G.; Spilker, A. *Ber. Bunsen-Ges. Phys. Chem.* **1896**, *29*, 552. (b) Wilder, P., Jr.; Culberson, C. F.; Youngblood, G. T. *J. Am. Chem. Soc.* **1959**, *81*, 655−658.

(5) Youngblood, G. T.; Trivette, C. D., Jr.; Wilder, P., Jr. *J. Org. Chem.* **1958**, *23*, 684−686.

(6) (a) Miller, J. B. *J. Org. Chem.* **1961**, *26*, 4905−4907. (b) Meinwald, J.; Meinwald, Y. C.; Baker, T. N., III. *J. Am. Chem. Soc.* **1963**, *85*, 2513−2514.

(7) (a) Swinehart, J. H.; Schmidt, W. G. *Inorg. Chem.* **1967**, *6*(2), 232−237. (b) Wolfe, S. K.; Swinehart, J. H. *Inorg. Chem.* **1968**, *7*(9), 1855−1859. (c) Butler, A. R.; Glidewell, C.; Chaipanich, V.; McGinnis, J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 7−9. (d) Butler, A. R.; Glidewell, C. *Chem. Soc. Rev.* **1987**, *16*, 361−380 and references therein.

(8) Bottomley, F.; White, P. S.; Mukaida, M.; Shimura, K.; Kakihana, H. *J. Chem. Soc., Dalton Trans.* **1988**, 2965−2969.

(9) (a) Bowden, W. L.; Little, W. F.; Meyer, T. J. Salmon, D. *J. Am. Chem. Soc.* **1975**, *97*, 6897−6898. (b) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 5605−5606. (c) Bowden, W. L.; Little, W. F.; Meyer, T. J. *J. Am. Chem. Soc.* **1976**, *98*, 444−448.

(10) Clamp, S.; Connelly, N. G.; Howard, J. A. K.; Manners, I.; Payne, J. D.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.* **1984**, 1659−1665.

(11) (a) Brunner, H. *J. Organomet. Chem.* **1968**, *12*, 517−522. (b) Brunner, H.; Loskot, S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 515−516. (c) Brunner, H.; Loskot, S. *J. Organomet. Chem.* **1973**, *61*, 401−414. (d) Becker, P. N.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 2985−2995. (e) Becker, P. N.; Bergman, R. G. *Organometallics* **1983**, *2*(7), 787−796.

(12) (a) Pilato, R. S.; McGettigan, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1990**, *9*, 312−317. (b) Mansuy, D.; Battioni, P.; Chottard, J.-C.; Riche, C.; Chiaroni, A. *J. Am. Chem. Soc.* **1983**, *105*, 455−463. (c) Weiner, W. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3922−3929. (d) Weiner, W. P.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 3612−3614. (e) Chang, J.; Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3258−3271. (f) Mansuy, D.; Dreme, M.; Chottard, J. C.; Guilhem, J. *J. Organomet. Chem.* **1978**, *161*, 207−220. (g) Mansuy, D.; Dreme, M.; Chottard, J.-C.; Girault, J.-P.; Guilhem, J. *J. Am. Chem. Soc.* **1980**, *102*, 844−845. (h) Sohl, C. D.; Lee, J.; Alguindigue, S. S.; Khan, M. A.; Richter-Addo, G. B. *J. Inorg. Biochem.* **2004**, *98*, 1238−1246.

(13) IR: KBr pellet, 2006 cm^{-1}; CH_3CN solution, 1953 cm^{-1}.

(14) $E_{1/2} = +0.96$ V vs Ag/AgCl in 1 M $HClO_4$. Compare with $E_{1/2} = -0.33$ V vs ferrocene in butyronitrile: Sieger, M.; Sarkar, B.; Zališ, S.; Fiedler, J.; Escola, N.; Doctorovich, F.; Olabe, J.; Kaim, W. *Dalton Trans.* **2004**, 1797−1800.

10.1021/om060141v CCC: $33.50

the most electrophilic species known to date. When *cis*-cyclooctene (or dicyclopentadiene) was added to an acetonitrile solution of K[$IrCl_5NO$] at room temperature, immediate formation of the corresponding coordinated *C*-nitroso compound was observed as a green precipitate.[15] After recrystallization and exchange of the potassium counterion by tetraphenylarsonium ($AsPh_4^+$), crystals of ($AsPh_4$)[*trans*-$IrCl_4(CH_3CN)$(*syn*-1-chloro-2-nitroso-1,2-dihydrodicyclopentadiene)] (**1**) suitable for X-ray diffraction were obtained (Figure 1).[16] Relevant structural parameters for this compound are shown in Table 1. Complete data are included as Supporting Information. Comparison with other complexes containing the $Ir^{III}Cl_4(NO)X$ moiety shows that the N−O and Ir−N distances as well as the Ir−N−O angle are in all cases very similar, including those for an HNO complex that was not described. Considering the above and the angle of 123.2° for Ir−N−O in **1**, a description of these complexes as $\{MNO\}^8$ could be suggested, according to the Enemark−Feltham notation.[17]

As described in the literature, in the observed products the C−Cl and C−N bonds are in a syn arrangement. The chloride added to the alkene could originate from a trans-labilized atom, from the same or another unit, or a cis atom that added concertedly with the nitrosyl. This latter mechanism is in agreement with one that is well established for this kind of addition.[18]

In the case of the reaction with dicyclopentadiene, NO adds to C1 or C2 indistinctly, producing 1:1 mixtures of two structural isomers (Figure 2). Each of these structural isomers are in fact racemic mixtures: (1*S*,2*R*)-1-chloro-2-nitroso-1,2-dihydropentadi-5-ene/(1*R*,2*S*)-1-chloro-2-nitroso-1,2-dihydropentadi-5-ene and (1*S*,2*R*)-1-chloro-2-nitroso-1,2-dihydropentadi-6-ene/(1*R*,2*S*)-1-chloro-2-nitroso-1,2-dihydropentadi-6-ene. In the present case, the stereoisomers are indistinguishable by X-ray diffraction analysis. The X-ray refinement shows almost identical lengths for the C30−C31 and C31−C32 bonds, shorter than for the rest of the C−C bonds. This is due to the presence of the isomers described above, in a 1:1 ratio. The ^1H NMR spectrum (see Figure SI5 in the Supporting Information) shows duplicated doublets for the methyne protons adjacent to the NO (H1 at 7.6 and 7.8 ppm) and the chloride (H2 at 4.3 and 4.4 ppm), the first one being shifted to a very high δ value. We also observe a more complex signal corresponding to the alkene protons, coupled between them and to a methylene and a methyne. At lower shifts appear the signals of the remaining methynes and the two methylenes. In the ^{13}C NMR spectra (see Figure SI6 in the Supporting Information), all signals appear duplicated. The methynes directly bonded to NO are shifted upward (δ 100.5 and 102.1 ppm) with respect to the standard values for methynes. The other ones, bonded to chloride, appear at lower δ values (57.7 and 60.4 ppm). Above 120 ppm, there are two sets of signals for the alkenyl carbons. This duplication of the NMR signals is due to the presence of the structural isomers shown in Figure 2. In the case of cyclooctene, only one set of signals was observed in the ^1H and ^{13}C NMR spectra, as expected for this symmetric compound (see the Supporting Information).

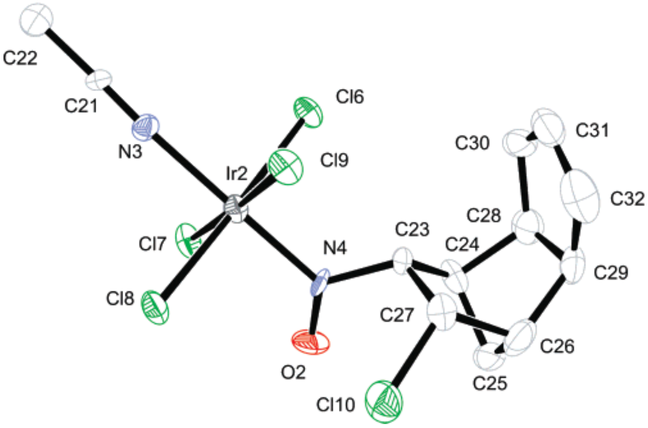

Figure 1. X-ray crystal structure and atom numbering for *trans*-[$IrCl_4(CH_3CN)$(*syn*-1-chloro-2-nitroso-1,2-dihydrodicyclopentadiene)]$^-$ (**1**). Thermal ellipsoids are drawn at the 50% probability level.

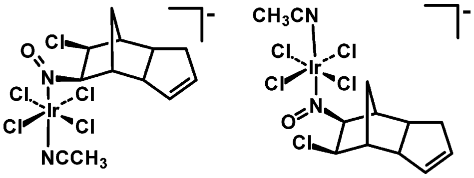

Figure 2. Two of the reaction products: *trans*-[$IrCl_4(CH_3CN)$(1*S*-chloro-2*R*-nitroso-1,2-dihydropentadi-5-ene) and (1*S*-chloro-2*R*-nitroso-1,2-dihydropentadi-5-ene).

In the case of the dicyclopentadiene products, ^{15}N-labeled compounds with the $Ir^{15}N(O)CR$ moiety were obtained by reaction of K[$IrCl_5{}^{15}NO$] with dicyclopentadiene, showing FTIR frequencies attributable to $C^{15}NO$ (ν_{NO}) at 1520 cm^{-1} for the unlabeled compounds and 1494 cm^{-1} for the labeled ones (Figure 3). In the case of 1-chloro-2-nitrosocyclooctene (**2**), ν_{NO} is found at 1529 cm^{-1}.

In the UV−vis spectra corresponding to the dicyclopentadiene products, a shift of the ^{1}MLCT band ($n_O \rightarrow \pi^*$) at 410 nm and the ^{3}MLCT band ($n_N \rightarrow \pi^*$, forbidden) at 618 nm to shorter wavelengths (20 and 54 nm, respectively) is observed by changing the solvent from acetonitrile to water. The solvent change also shifts, but in the opposite direction, the UV band assigned to the ligand ($\pi \rightarrow \pi^*$, from 207 to 230 nm). The negative mode high-resolution mass spectrum (ESI-MS) shows the molecular anion without the coordinated acetonitrile, [M − $CH_3CN]^-$, with the formula $C_{10}H_{12}Cl_5IrNO$ (*m*/*z* 531.89). We also observe with appreciable intensity an ion at *m*/*z* 506.94 corresponding to [M − Cl − NO − H]$^-$, with the formula $C_{12}H_{14}Cl_4IrN$, formed by loss of NO and HCl. In the MS/MS spectra of the molecular ion we observed the loss of the carbonated fragment, which is replaced by the anion [$IrCl_5NO]^-$, *m*/*z* 399.93, by breakage of the C−N bond. In the MS/MS

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[15] A 0.046 mmol amount of the corresponding alkene was added under an Ar atmosphere at room temperature to 10 mg (0.023 mmol) of K[$IrCl_5$(NO)] in 0.25 mL of acetonitrile. The green product which precipitated immediately was separated from the solution by centrifugation (ca. 90% yield). The tetraphenylphosphonium salt was obtained by adding a saturated aqueous solution (red) of the crude product to an ethanolic saturated solution of tetraphenylphosphonium chloride. The tetraphenylarsonium salt was obtained by adding a saturated aqueous solution (red) of the crude product to a saturated acetonitrile solution of tetraphenylarsonium bromide. In both cases, after slow evaporation of the supernatant, the green crystals thus produced were separated by centrifugation and carefully dried. The dry product was dissolved in warm acetonitrile (60 °C), and this solution was allowed to reach room temperature very slowly. The crystals obtained in this way were suitable for X-ray analysis in the case of dicyclopentadiene. Anal. Calcd for K[$IrCl_4(NCCH_3)(N(O)C_8H_{14}Cl)$]: C, 20.4; H, 2.9; N, 4.7. Found: C, 20.1; H, 3.0; N, 4.5. Anal. Calcd for (PPh_4)[$IrCl_4(NCCH_3)(N(O)$-$C_{10}H_{12}Cl)$]: C, 47.4; H, 3.9; N, 3.1. Found: C, 48.5; H, 3.9; N, 2.9 (this last high value for C might be due to a small amount of PPh_4Cl present as an impurity).

[16] Crystal data: $C_{36}H_{34}AsCl_5IrN_2O$, M_r = 955.02, specimen 0.6 × 0.2 × 0.1 mm, triclinic, space group $P\bar{1}$, a = 9.5360(19) Å, b = 13.146(3) Å, c = 28.721(6) Å, β = 92.09(3)°, $F(000)$ = 1868, V = 3586.7(12) Å^3, T = 120(2) K, Z = 4, D_c = 1.769 Mg/m^3, μ = 5.043 mm^{-1}. Refinement method: full-matrix least squares on F^2, R = 0.0430, R_w = 0.0356 (observed data with $I > 2\sigma(I)$).

[17] Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339−406.

[18] Youngblood, G. T.; Trivette, C. D., Jr.; Wilder, P., Jr. *J. Org. Chem.* **1958**, *23*(5), 684−686. Miller, J. B. *J. Org. Chem.* **1961**, *26*(12), 4905−4907.

Table 1. Selected Bond Lengths (Å) and Angles (deg)

	1	K[IrCl$_4$(CH$_3$CN)-N(O)SCH$_2$Ph][19]	[IrCl$_5$(*N*-nitroso-*p*-toluidine)]$^{2-}$ [20]	(PPh$_4$)-[IrCl$_5$NO]	[IrCl$_5$-(HNO)]$^{2-}$ [a]
		Bond Lengths			
N4−O2	1.216(8)	1.22	1.225	1.214	1.225
C23−N4	1.494(9)				
N4−Ir2	1.948(6)	1.96	1.992	1.745	1.900
N3−Ir2	2.066(7)	2.03			
C30−C31	1.387(13)				
C31−C32	1.390(14)				
		Bond Angles			
O2−N4−Ir2	123.2(5)	124.1	124.9	149.5	134.2
O2−N4−C23	117.3(6)				
Ir2−N4−C23	119.1(5)				
N4−C23−C27−Cl10	11.2(9)				

[a] Calculated by DFT (G98 software package).[21] Fully optimized geometry at the B3LYP[22] level with a double-ζ plus polarization (DZPV) basis set[23] for N, O, H, and Cl atoms and the LANL2DZ basis set and effective core potential for Ir.[24]

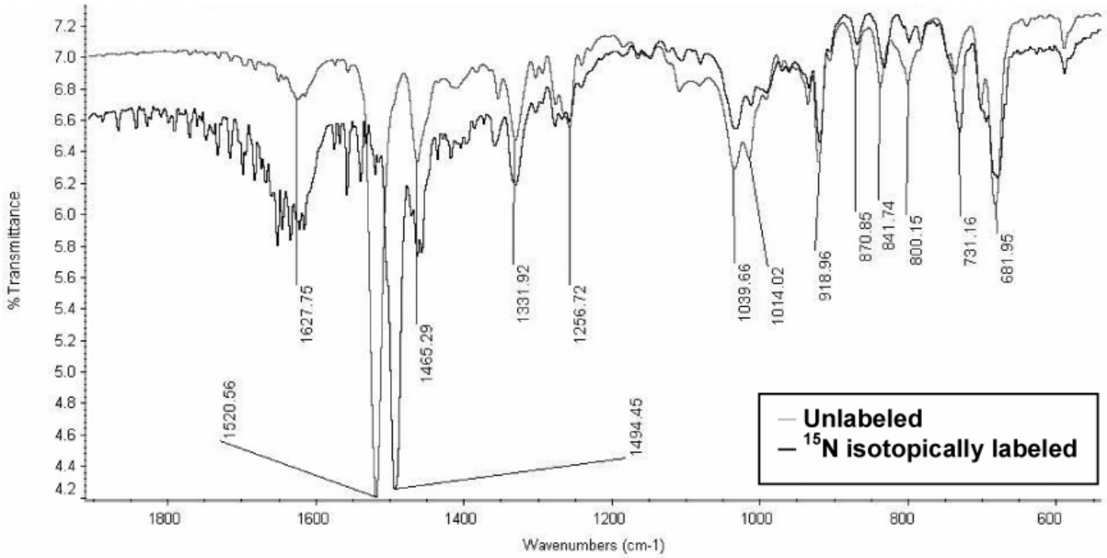
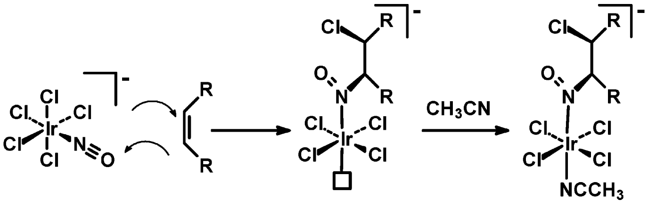


Figure 3. FTIR spectra for the unlabeled (light black line) and ^{15}N isotopically labeled (thick black line) complexes (**1**).

Scheme 1



spectrum of the ion with *m*/*z* 506.94, the ion [M − Cl − NO − H − CH$_3$CN]$^-$, *m*/*z* 468.95, was seen.

Formation of the products by electrophilic addition is shown in Scheme 1. Initial nucleophilic attack by the alkene is followed by immediate or simultaneous syn addition of chloride. The chloride located trans to NO is labilized and replaced by an acetonitrile molecule.

In summary, we have shown the facile formation of monomeric *C*-nitroso compounds which remain stabilized by coordination and can be easily crystallized, as some of the few examples of electrophilic addition of coordinated NO to an alkene. This could be achieved thanks to the high electrophilicity, due to very weak back-bonding, and the inertness of the [IrCl$_5$]$^{2-}$ moiety. These two qualities, generally not compatible, define the anion [IrCl$_5$NO]$^-$ as a rather unique reagent. Other alkenes,[25] substituted by attracting groups such as nitriles or carboxylates, do not react under the conditions described herein.

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Supporting Information Available: A CIF file giving complete crystallographic data, text giving experimental procedures, and figures giving NMR, ESI-MS, ESI MS-MS, and UV−visible spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Perissinotti, L. L.; Estrin, D. A.; Leitus, G.; Doctorovich, F. *J. Am. Chem. Soc.* **2006**, *128*, 2512−2513.

(20) Doctorovich, F.; Di Salvo, F.; Escola, N.; Trápani, C.; Shimon, L. *Organometallics*, **2005**, *24*, 4707−4709.

(21) Frisch, M. J.; et al. *Gaussian 98*, Rev. A7; Gaussian, Inc., Pittsburgh, PA, 1998. See the Supporting Information for the remaining 56 authors.

(22) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. Lee, C.; Yang, W.; Parr, R., *Phys. Rev.* **1988**, *B37*, 785−789.

(23) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560−571.

(24) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310.

(25) The unreactive alkenes (and one alkyne) are as follows: fumaric acid, *trans*-cinnamic acid, citraconic acid, 2,3-dimethylmaleic anhydride, 2,4-hexadienoic acid, *cis*-2-pentenenitrile, 2-butinoic acid, and tetracyanoethylene.