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Preliminary communication

Carbon–hydrogen activation by metal carbonyl complexes induced by dinitrogen monoxide *

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Abstract

Dicarbonyl{tris(3,5-dimethylpyrazol-1-yl)hydridoborato}rhodium (1) activates cyclohexane or benzene solvents when purged in the dark with N_2O at 25 °C and 1 atm. Nitrous oxide induced activation of these solvents by $[Ir(\eta\text{-}C_5Me_5)(CO)_2]$ (2) requires higher temperature and pressure; in cyclohexane at 125 °C and 50 atm the yield of $[Ir(\eta\text{-}C_5Me_5)(H)(C_6H_{11})(CO)]$ is 76% at 59% conversion in 1 h. Abstraction of the CO ligand in these reactions is proposed to involve a metallacyclic intermediate (unobserved) formed by attack of N_2O as a 1,3-dipolar reagent on the metal–carbon bond.

Reactive intermediates capable of intermolecular C–H activation may be formed in various non-photochemical processes. These include (a) the reduction of complexes such as $[RuCl_2(Me_2PCH_2CH_2PMe_2)_2]$ or $[OsI_2(\eta\text{-}C_6H_6)(PR_3)]$ with sodium naphthalenide [1,2]; (b) reductive elimination of RH from complexes such as $[M(\eta\text{-}C_5Me_5)(H)(R)PMe_3]$ (M = Rh, Ir) with RH frequently an alkane [3,4]; (c) loss of a ligand such as olefin, as in the case of benzene activation by $[Rh(HBPz^{\star}_3)(CO)(\eta^2\text{-}C_2H_4)]$ ($Pz^{\star}$ = 3,5-dimethylpyrazol-1-yl) [5].

In electron-rich metal carbonyl complexes likely to produce stable C–H activation products, M–CO bond strengths are high and photochemical techniques are often (although not invariably [5]) used to generate the reactive intermediate, as in the case of $[Ir(\eta\text{-}C_5Me_5)(CO)_2]$ and $[Ir(\eta\text{-}C_5H_5)(CO)_2]$ [6]. The latter complexes were unreactive towards trimethylamine oxide [7], which therefore did not afford a non-photochemical, "chemically assisted' pathway to C–H activation using these complexes. We were thus intrigued by the use of arylnitrile oxides (1,3-dipolar

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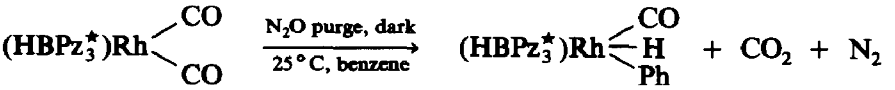
* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

reagents such as p-$\mathrm{ClC_6H_4{-}\overset{(+)}{N}{\equiv}C{-}\overset{(-)}{O}}$) to remove CO from an anionic carbonyl complex [8] and their subsequent use to bring about C–H activation in the dark by $[\mathrm{Ir}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$ and $[\mathrm{Rh}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})(\mathrm{PMe_3})]$ [9].

We have examined CO removal by a familiar 1,3-dipolar reagent, dinitrogen oxide, $\mathrm{N_2O}$ (viewed as $:\overset{(+)}{\mathrm{N}}{=}\overset{(-)}{\ddot{\mathrm{N}}}{-}\mathrm{O}$ in this context [10]) and summarize our findings here for two complexes, $[\mathrm{Rh}(\mathrm{HBPz}^{\star}_3)(\mathrm{CO})_2]$ (**1**) and $[\mathrm{Ir}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{CO})_2]$ (**2**), which are known to activate C–H bonds photochemically [6,11].

When a benzene solution of **1** (2.2 mM) was purged in the dark with $\mathrm{N_2O}$ by means of a glass frit at 1 atm and 25 °C, reaction according to eq. 1 is complete in 4.5 h.



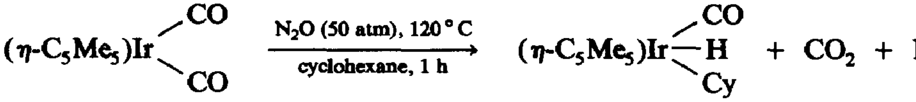
$$(\mathrm{HBPz}^{\star}_3)\mathrm{Rh}\begin{matrix}\diagup \mathrm{CO}\\ \diagdown \mathrm{CO}\end{matrix} \xrightarrow[25\,^\circ\mathrm{C,\ benzene}]{\mathrm{N_2O\ purge,\ dark}} (\mathrm{HBPz}^{\star}_3)\mathrm{Rh}\begin{matrix}\diagup \mathrm{CO}\\ - \mathrm{H}\\ \diagdown \mathrm{Ph}\end{matrix} + \mathrm{CO_2} + \mathrm{N_2} \qquad (1)$$

(**1**) (**3**)

From IR intensity measurements, conversion of **1** to the known complex **3** [11] was quantitative. The $\mathrm{CO_2}$ product was confirmed by passing the effluent gas through aqueous $\mathrm{Ba(OH)_2}$.

Reaction of **1** with $\mathrm{N_2O}$ in cyclohexane under the same conditions afforded $[\mathrm{Rh}(\mathrm{HBPz}^{\star}_3)(\mathrm{H})(\mathrm{Cy})(\mathrm{CO})]$ (**4**, Cy = cyclohexyl), identified after 20 minutes by its carbonyl stretching band at 2028 $\mathrm{cm^{-1}}$. Complex **1** had reacted completely within 7 h, but as reported for the photochemical reaction [11], the initial product **4** decomposes over several hours in cyclohexane forming low yields of species having $\nu(\mathrm{CO})$ at 2048 and 2041 $\mathrm{cm^{-1}}$; only the latter bands (now known to be due to **3** and $[\mathrm{Rh}(\mathrm{HBPz}^{\star}_3)(\mathrm{CO})\mathrm{H_2}]$) remained at the end of the reaction.

More vigorous conditions were required for $\mathrm{N_2O}$-assisted C–H activation using the iridium complex **2**. Solutions of **2** (80–100 mg in 40–50 mL cyclohexane, ca. 5 mM) were placed in a 200 mL stainless steel autoclave which was purged once with $\mathrm{N_2O}$, pressurized to 50 atm, and immersed to about half its height in an oil bath at the indicated temperature; working pressures at 100 °C were ca. 75 atm. Reaction took place according to eq. 2, and under the optimized conditions shown, the yield of the known [6a] product **5** is 76% at 59% conversion. Under comparable conditions, $[\mathrm{Ir}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]$ did not react with $\mathrm{N_2O}$.

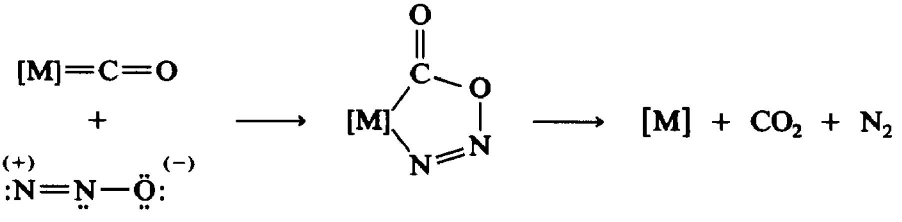


$$(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ir}\begin{matrix}\diagup \mathrm{CO}\\ \diagdown \mathrm{CO}\end{matrix} \xrightarrow[\mathrm{cyclohexane,\ 1\ h}]{\mathrm{N_2O\ (50\ atm),\ 120\,^\circ C}} (\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ir}\begin{matrix}\diagup \mathrm{CO}\\ - \mathrm{H}\\ \diagdown \mathrm{Cy}\end{matrix} + \mathrm{CO_2} + \mathrm{N_2} \qquad (2)$$

(**2**) (**5**)

The $\mathrm{N_2O}$–**2** system also activates benzene, forming the known $[\mathrm{Ir}(\eta\text{-}\mathrm{C_5Me_5})(\mathrm{H})(\mathrm{Ph})(\mathrm{CO})]$. This reaction has not been systematically investigated, but at 50 atm and 68 °C for 21 h the yield was ca. 50% at 20% conversion. Smaller amounts of an unidentified product having $\nu(\mathrm{CO})$ at 1743 $\mathrm{cm^{-1}}$ (in n-hexane) were also formed.

We presume that a metallacycle of the type shown in eq. 3 is involved in these reactions, although no spectroscopic evidence was obtained for such an intermediate.



(3)

This is in contrast to the adducts of arylnitrile oxides and metal carbonyl complexes investigated by Hawthorne et al. [8,9,12] for which various metallacyclic intermediates have been fully characterized. The failure of $[Ir(\eta-C_5H_5)(CO)_2]$ (ν(CO) 2041, 1974 cm^{-1}, hexane) to react as does **2** (ν(CO) 2019, 1953 cm^{-1}, hexane) is consistent with formal 1,3-dipolar addition to the metal–carbon double bond. Higher ν(CO) in the η-C_5H_5 derivative of course implies less metal–carbon double bond character, which is the basis for the analogy with a carbon–carbon double bond implied by eq. 3.

The scope of the N_2O reaction for removal of a CO ligand has not been established, but like the arylnitrile oxides its reactivity should be complementary to that of Me_3NO [13]. Dinitrogen oxide has high solubility in hydrocarbons (0.14 *M* in n-hexane at 25 °C and 1 atm [14]) and is of course readily available. It appears less reactive than representative arylnitrile oxides [12], which react with **2** over 5–8 h at room temperature. The relatively high stability of the metallacycle and η^2-nitrile intermediates formed from nitrile oxides appears, however, to limit the yield in thermal cyclohexane activation.

Dinitrogen monoxide has been utilized in the synthesis of organometallic oxo compounds [15] and has been shown to oxidize several organometallic ligands such as phenyl or coordinated cyclohexyne [16]. To our knowledge, the work reported here is the first example in which coordinated carbon monoxide is oxidized.

Cautionary note. Although no difficulty was experienced in this work, N_2O is an oxidizing agent and large amounts are dissolved in the hydrocarbon solvents at the pressures utilized. Appropriate precautions should be taken in view of the thermodynamic instability of these mixtures.

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References

1 J. Chatt and J.M. Davidson, J. Chem. Soc., (1965) 843.
2 H. Werner, H. Kletzin and K. Roder, J. Organomet. Chem., 355 (1988) 401.
3 J.M. Buchanan, J.M. Stryker and R.G. Bergman, J. Am. Chem. Soc., 108 (1986) 1537.
4 W.D. Jones and F.J. Feher, J. Am. Chem. Soc., 106 (1984) 1650.
5 C.K. Ghosh, D.P.S. Rodgers and W.A.G. Graham, J. Chem. Soc., Chem. Commun., (1988) 1511.
6 (a) J.K. Hoyano and W.A.G. Graham, J. Am. Chem. Soc., 104 (1982) 3723; (b) J.K. Hoyano, A.D. McMaster and W.A.G. Graham, J. Am. Chem. Soc., 105 (1983) 7190.

7 J.K. Hoyano, unpublished observations.
8 J.A. Walker, C.B. Knobler and M.F. Hawthorne, J. Am. Chem. Soc., 105 (1983) 3370.
9 P.A. Chetcuti, C.B. Knobler and M.F. Hawthorne, Organometallics, 5 (1986) 1913; P.A. Chetcuti and M.F. Hawthorne, J. Am. Chem. Soc., 109 (1987) 942; P.A. Chetcuti, C.B. Knobler and M.F. Hawthorne, Organometallics, 7 (1988) 650.
10 R. Huisgen, Angew. Chem. Int. Ed. Engl., 2 (1963) 565.
11 C.K. Ghosh and W.A.G. Graham, J. Am. Chem. Soc., 109 (1987) 4726.
12 P.A. Chetcuti, J.A. Walker, C.B. Knobler and M.F. Hawthorne, Organometallics, 7 (1988) 641.
13 T.Y. Luh, Coord. Chem. Rev., 60 (1984) 255; M.O. Albers and N.J. Coville, Coord. Chem. Rev., 53 (1984) 227.
14 C.L. Young (Ed.), Oxides of Nitrogen, IUPAC Solubility Data Series, Vol. 8, Pergamon Press, Oxford, 1981
15 F. Bottomley and L. Sutin, Adv. Organomet. Chem., 28 (1988) 339.
16 G.A. Vaughan, C.D. Sofield and G.L. Hillhouse, J. Am. Chem. Soc., 111 (1989) 5491.