Inorganica Chimica Acta, 35 (1979) L301–L302
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Reactivity of $M(ArN{-}N{=}NAr)(CO)(PPh_3)_2$ with Aryldiazonium Salts (M = Rh(I), Ir(I); Ar = $p\text{-}CH_3C_6H_4$, $p\text{-}FC_6H_4$)

LUIGI TONIOLO* and GIANNI CAVINATO

Istituto di Chimica Generale ed Inorganica e di Chimica Inorganica Industriale, The University, Padua, Italy

Received February 1, 1979

The chemistry of aryldiazenido transition metal complexes is of increasing current interest because such complexes have been proposed as single models of nitrogen-fixing enzymes [1] because of the coordination modes available to the ligand [2] and for the variety of products that they may generate [3].

This last point is well illustrated by the products of the reaction of $IrCl(CO)(PPh_3)_2$ with aryldiazonium cations. Thus, for example, in benzene–acetone the diazonium ion oxidatively adds to produce iridium (III) aryldiazenido-complexes only if the aromatic ring is substituted by a strong electron-withdrawing group, such as NO_2 [4]; in benzene–ethanol the reactions are not restricted to such a class of diazonium cations, and the products are the complex $IrCl_2(N_2Ar)(CO)(PPh_3)_2$, the orthometallated arylhydrazido-complex $[Ir(NHNHAr)(CO)(PPh_3)_2][BF_4]$, the orthometallated aryldiazene-complex $[IrX(NHNAr)(CO)(PPh_3)_2]BF_4$ and the aryltetrazenido-complex $[Ir(N_4Ar_2)(CO)(PPh_3)_2][BF_4]$ [3].

The rhodium(I) analog does not yield aryldiazenido derivatives under similar conditions.

We have found that the title complexes, obtained from $MCl(CO)(PPh_3)_2$ by substitution of Cl^- with $(ArN{\cdots}N{\cdots}NAr)^-$, easily react with $[ArN_2][BF_4]$, both in benzene–acetone or –ethanol medium, following reactions 1 and 2:

$$Ir(ArN{\cdots}N{\cdots}NAr)(CO)(PPh_3)_2 + [ArN_2][BF_4] \rightarrow \underset{(A)}{[Ir(ArN{\cdots}N{\cdots}NAr)(CO)(PPh_3)_2][BF_4]} \qquad (1)$$

$$Rh(ArN{\cdots}N{\cdots}NAr)(CO)(PPh_3)_2 + [ArN_2][BF_4] \rightarrow \underset{(B)}{[Rh(OC{-}N(Ar){-}N{=}NAr)(N_2Ar)(PPh_3)_2][BF_4]} \qquad (2)$$

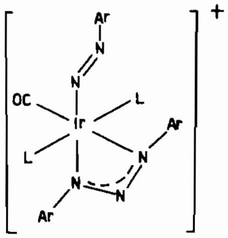
The i.r. spectrum of the product of reaction 1 shows one band for ν(C≡O) at *ca.* 2060 cm^{-1} typical of an iridium(III) aryldiazenido- or aryldiazene-complex [3]. However, the fact that i) no ν(N–H) band and ii) no ^1H n.m.r. signal assignable to a nitrogen bonded proton could be detected, suggests that reaction 1 leads to an aryldiazenido-complex. Moreover, although in principle the formation of an aryldiazene-complex is possible, as observed in reactions of $IrCl(CO)(PPh_3)_2$ with diazonium salts in the presence of a hydrogen donor alcohol such as ethanol or isopropanol *via* initial formation of an aryldiazenido intermediate [3], it must be observed that reaction 1 readily occurs also in the absence of such alcohols, for example in benzene–acetone, where the formation of aryldiazene-complexes is not expected to occur [3].

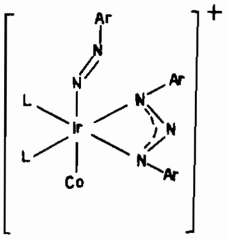
In the 1600–1400 cm^{-1} region, where ν(N=N) usually occurs in such type of complexes [5] there are several bands, but the exact assignment by isotopic substitution has not been carried out. The i.r. absorption bands for the 1,3-diaryltriazenido ligand have been characterized into two classes [6]. One class shows bands at *ca.* 1300–1260 cm^{-1} for the ligand acting as chelating; the other class shows bands also at 1380–1360, 1220 and 1150 cm^{-1} for the ligand acting as monodentate [6].

Complex (A) shows bands of very weak intensity at *ca.* 1200 and 1160 cm^{-1} and bands of strong intensity at *ca.* 1300 cm^{-1} suggesting that the triazenido ligand acts as chelating. Moreover, upon treatment with LiCl, complex (A) is recovered unreacted, suggesting that there are no coordination sites available to the Cl^- anion. This fact further supports the formulation of (A) as having a chelating triazenido ligand in a six-coordinated iridium(III)-aryldiazenido-complex. A chelating structure for the triazenido ligand, forming a four-membered ring with the metal and presenting considerable angular tension, has been already unambiguously established by X-ray diffraction studies [7].

The ^1H n.m.r. spectrum of complex (A) for Ar = $p\text{-}CH_3C_6H_4$ shows only one signal in the methyl protons region at *ca.* τ 7.6 even at low temperature (–80 °C in CD_2Cl_2): this might be due to casual superimposition of the signals.

Possible arrangements for complex (A) which present a 'doubly bent' Ir–N=N linkage analogously to what has been unambiguously established by X-ray diffraction studies for $IrCl_2(N{=}NC_6H_4NO_2\text{-}o)(CO)(PPh_3)_2$ [8] are the following:





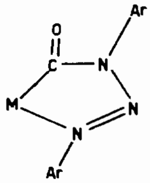
It is interesting to underline that $[ArN_2][BF_4]$ (Ar = $p\text{-}CH_3C_6H_4$, $p\text{-}FC_6H_4$) adds to $IrCl(CO)(PPh_3)_2$

---

*Author to whom correspondence should be addressed in benzene–acetone only in the presence of a coordinating ligand such as Cl^- to yield $IrCl_2(N_2Ar)(CO)(PPh_3)_2$ [4]. Probably the chelating capacity of the triazenido ligand facilitates reaction 1.

The i.r. spectrum of the product of reaction 2 shows no band in the 2300–1950 cm^{-1} region (for $\nu(N\equiv N)$ and $\nu(C\equiv O)$ of the starting compounds), whilst it shows bands of strong intensity at *ca.* 1690, 1630 and 1590 cm^{-1} and several bands in the 1320–1160 cm^{-1} region. The band at 1690 cm^{-1} is assignable to $\nu(C{=}O)$ of an acyltriazenido ligand yielded by (formal) CO insertion into a Rh–N bond of the triazenido ligand. Such insertion has been already shown to occur with $MX(CO)(PR_3)_2$ (M = Rh(I) and Ir(I); X = Cl, CF_3COO) and HgX′(tri) (X′ = Cl, I) [9] and with $Ir(tri)(CO)(PPh_3)_2$ and CO [10] (tri = triazenido ligand): in these cases $\nu(C{=}O)$ occurs in the 1730–1650 cm^{-1} region for an acyltriazenido chelating ligand. The bands in the 1320–1160 cm^{-1} region might be associated with the remaining triazenido linkage [9]. The bands at 1630 and 1590 cm^{-1} are tentatively assigned to $\nu(N{=}N)$ of the aryldiazenido ligand, for other aryldiazenido complexes of rhodium(III) show $\nu(N{=}N)$ in that region [11, 12].

A possible arrangement for the acyltriazenido linkage is:



The ¹H n.m.r. spectrum of complex (B) in the methyl resonance region is rather complex and varies with time, suggesting that some decomposition (or rearrangement) takes place.

It is interesting to observe that $RhCl(CO)(PPh_3)_2$ does not yield aryldiazenido complexes in reactions with $[ArN_2][BF_4]$, while $RhCl(PPh_3)_3$ easily yields $RhCl_2(N_2Ar)(PPh_3)_2$ [11, 12]. Probably in reaction 2 the removal of CO to form a chelating acyltriazenido ligand facilitates the formation of (B).

Acknowledgments

The authors thank the Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Padua, Italy, for financial support.

References

1 G. W. Parshall, *J. Am. Chem. Soc., 89,* 1822 (1967).
2 A. P. Gaughan, B. L. Haymore, J. A. Ibers, W. H. Meyers, T. E. Nappier and D. W. Meek, *J. Am. Chem. Soc., 95,* 6859 (1973).
3 N. Farrel and D. Sutton, *J. Chem. Soc. Dalton,* 2124 (1977).
4 L. Toniolo, *Chem. Ind.,* 30 (1976).
5 B. L. Haymore, J. A. Ibers and D. W. Meek, *Inorg. Chem., 14,* 541 (1975).
6 E. Pfeiffer, A. Oskam and K. Vrieze, *Trans. Met. Chem., 2,* 240 (1977).
7 a) A. M. Corbett and B. F. Hoskins, *J. Am. Chem. Soc., 89,* 1530 (1967).
b) B. L. D. Brown and J. A. Ibers, *Inorg. Chem., 15,* 2788 (1976).
8 R. E. Cobbledick, F. W. B. Einstein, N. Farrel, A. B. Gilchrist and D. Sutton, *J. Chem. Soc. Dalton,* 373 (1977).
9 P. I. van Vliet, J. Kuyper and K. Vrieze, *J. Organomet. Chem., 122,* 99 (1976).
10 J. Kuyper, P. I. van Vliet and K. Vrieze, *J. Organomet. Chem., 105,* 379 (1976).
11 K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc. Dalton,* 2713 (1973).
12 L. Toniolo, G. De Luca, C. Panattoni and G. Deganello, *Gazz. Chim. Ital., 104,* 961 (1974).