

Electron Transfer from Tetracarbonylrhodate(1-) to Nitro Aromatics: Novel Interaction of Nitro Radical Anions with a Rhodium(I) Centre

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Treatment of $\text{PPN}[\text{Rh}(\text{CO})_4]$ [$\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}$] with various nitro-aromatics in THF at ambient temperature produces a new class of neutral radicals; rhodium(I) species consisting of two *cis* carbonyl ligands and a bidentate aromatic nitro radical anion of which the nitro group and an *ipso-ortho* carbon double bond on the ring are bound to the rhodium centre.

The reduction of nitro aromatics generally occurs *via* electron transfer from a reductant to a nitro compound¹ in the first step. Extensive studies by EPR spectroscopy^{1,2} on electron-transfer reactions has led to the establishment of nitro radical anions as one of the largest classes of radicals known. An important aspect of these studies is the interaction of nitro radical anions with solvents and counter cations,³ but the only known interaction of nitro radical anions with cations is limited to simple ion-pairing. Transition metal carbonyls are known to reduce aromatic nitro compounds^{4,5} and electron transfer has been observed in these reactions.^{6,7,8} Our interest in organometallic radicals,⁹ and in the chemistry and catalytic activities of $\text{Rh}(\text{CO})_4^-$,¹⁰ prompted us to explore systematically the reaction of $\text{Rh}(\text{CO})_4^-$ with aromatic nitro compounds by EPR spectroscopy. Here we report the electron transfer between $\text{Rh}(\text{CO})_4^-$ and aromatic nitro compounds and the observation of a new class of nitro radical anions that act as bidentate ligands coordinated to a rhodium centre.

The reaction of $\text{PPN}[\text{Rh}(\text{CO})_4]$ ¹¹ [5.31×10^{-2} mmol; $\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}$] with 4-chloronitrobenzene (1.39×10^{-3} mmol) in THF (0.80 ml) at 223 K produced an EPR† signal [Fig. 1(a)] that, based on the *g* value (2.0052) and hyperfine coupling constants, is assigned as the free or ion-paired radical anion of 4-chloronitrobenzene **I**.¹² As the concentration ratio of 4-chloronitrobenzene to $\text{Rh}(\text{CO})_4^-$ was increased and as the reaction temperature was raised, a new radical **II** at *g* = 2.0011 appeared in addition to **I**. Only the new radical was observed [Fig. 1(b)] at 293 K with $\text{Rh}(\text{CO})_4^-$:4-chloronitrobenzene = 1:3. Radical **II** disappeared gradually with a half-life *ca.* 0.5 h at ambient temperature. Analysis of this EPR spectrum indicates that the signal is a 4-chloronitrobenzene-based radical with hyperfine coupling constants of 8.90, 3.85 and 1.35 G (1 G = 10^{-4} T) for the nitrogen of the nitro group, an *ortho* proton and two *meta* protons, respectively. Surprisingly, only one of the two *ortho* protons shows hyperfine interaction, revealing an unsymmetrical spin density distribution on the aromatic ring. The assignment is supported by the observation that similar unsymmetrical radicals **III–V** were also observed from the

reaction of $\text{PPN}[\text{Rh}(\text{CO})_4]$ with symmetrically substituted aromatic nitro compounds 3,5-dichloronitrobenzene, 4-nitrobenzonitrile and methyl 4-nitrobenzoate, respectively. For all these nitro radicals, only one *ortho* proton on each aromatic ring reveals hyperfine coupling with the unpaired electron; the hyperfine interaction of the second *ortho* hydrogen is too small to be resolved. For the 4-nitrobenzonitrile radical, the nitrogen on the cyano group also exhibits substantial hyperfine interaction with a coupling constant of 0.74 G. These unsymmetrical radicals show significant small *g* values (2.001 *cf.* 2.005) and large hyperfine coupling constants for the *ortho*, *meta* and *para* protons on the aromatic ring, relative to EPR data of the corresponding free aromatic nitro radical anions.^{12,13} The reaction of nitrobenzene with $\text{PPN}[\text{Rh}(\text{CO})_4]$ also produced an unsymmetrical nitrobenzene radical **VI**, but unlike the other unsymmetrical radicals, the hyperfine coupling constants for both *ortho* protons were resolved, with one (3.80 G) much greater than the other (0.40 G), in addition to those for the *meta* and *para* protons and the nitrogen atom.

The observation of two different hyperfine constants for the *ortho* hydrogens in each unsymmetrical radical strongly

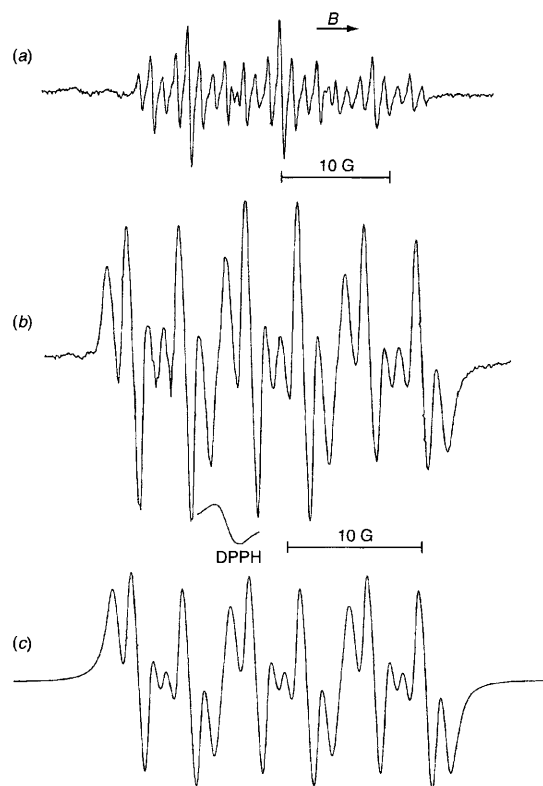
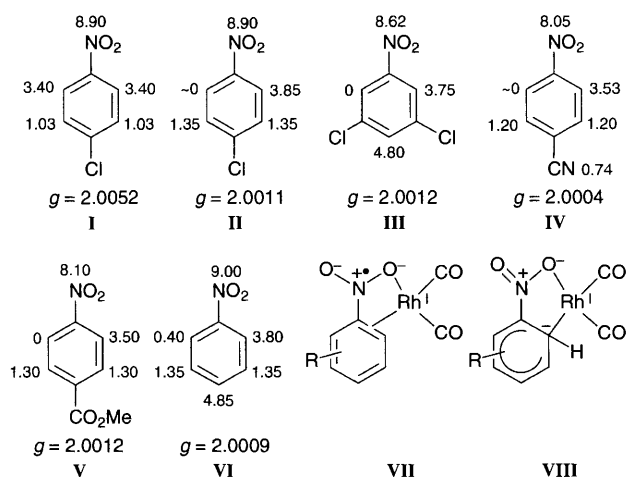


Fig. 1 EPR spectra from the reaction of 4-chloronitrobenzene with $\text{PPN}[\text{Rh}(\text{CO})_4]$ (a) at 223 K with a molar ratio $\text{Rh}(\text{CO})_4^-$:4- $\text{ClC}_6\text{H}_4\text{NO}_2$ = 38.3:1 showing the presence of the free 4-chloronitrobenzene radical anion **I**, (b) at 293 K with a molar ratio of $\text{Rh}(\text{CO})_4^-$:4- $\text{ClC}_6\text{H}_4\text{NO}_2$ = 1:3 showing the presence of an unsymmetrical radical **II** of 4-chloronitrobenzene and (c) a simulation spectrum of the radical observed in (b) using the parameters 8.90 ($I = 1, 1$), 3.85 ($I = 1/2, 1$) and 1.35 G ($I = 1/2, 2$)

indicates the interaction of a rhodium fragment with the aromatic ring at an *ortho* position. Direct evidence for the presence of a rhodium fragment comes from isotope labeling studies. Treatment of $\text{PPN}[\text{Rh}(\text{}^{13}\text{CO})_4]$ with 4-chloronitrobenzene at 293 K afforded a radical [Fig. 2(a)] with a g value the same as that of **II** within experimental error. Moreover, spectral analysis and simulation [Fig. 2(b)] reveals that the radical consists of two extra hyperfine coupling constants (1.56 and 0.98 G) in addition to those observed for **II**. Similarly, the reaction of $\text{PPN}[\text{Rh}(\text{}^{13}\text{CO})_4]$ with nitrobenzene at 293 K produced an EPR signal of which the g value and the hyperfine coupling constants are the same (within experimental error) as those for **VI** except for the two extra hyperfine constants (1.59 and 0.95 G). In view of the absence of hyperfine coupling of rhodium in **II–VI**, the extra hyperfine coupling constants are assigned to two ^{13}CO groups coordinated to the rhodium centre. Based on the above observations and the requirement that the rhodium fragment should be an even-electron system in order for **II–VI** to be radicals, we propose that these radicals are neutral square-planar rhodium(I) species consisting of two *cis* carbonyls and a coordinated nitro radical anion of which an oxygen of the nitro group and a double bond between the *ipso* and *ortho* carbons on the aromatic ring are bound to the rhodium centre (structure **VII**). An alternative structure (**VIII**) involving a σ -bond to an *ortho* carbon atom and thus a five-membered metallacycle is less likely due to the break-down of aromaticity, high negative charge density on the coordinated *ortho* carbon instead of the nitro group and the expected high spin density which was not observed on the *meta* carbons. Other structures such as a tetrahedral rhodium complex or a cluster will not lead to two different carbonyl ligands. It is noteworthy that square-planar rhodium(I) complexes with two *cis* carbonyls, an anionic ligand and a neutral ligand (alkene, amine *etc.*) similar to **VII** are known,^{14,7} and intramolecular η^2 -arene metal complexes analogous to **VII** in stereo arrangement were also reported.¹⁵

Clearly, the η^2 -coordination of the aromatic ring in **VII** drastically reduces the spin density on the *ortho* carbon bound to the metal. The spin density originally on this *ortho* carbon of the free radical anion then shifts to the other carbons on the ring leading to substantial increase of the spin density on these carbons and, to a less extent, shifts to the two carbonyls attached to the rhodium metal. At present, however, the cause for the observed change of spin density of the nitro radical anions on coordination to the Ru^I centre is not understood.

The observed unsymmetrical nitro radicals are the first examples involving not only the interaction of a nitro group, but

also the aromatic ring with a metal fragment. The structure determination of these radicals greatly widens our understanding of the interaction of an aromatic nitro radical anion with its counter cation. Finally, it is noteworthy that such types of radicals were proposed to be a key intermediate in the reductive carbonylation of aromatic nitro compounds catalysed by rhodium carbonyl complexes.^{7‡}

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Footnotes

† EPR spectra were measured on a Bruker 200 D 10/12 spectrometer, while simulations were performed on an Aspect 2000 computer using the software EPRSRC.015.

‡ A nitrogen-centred radical ($a_{\text{N}} = 8.8$ G; $a_{\text{H}} = 3.9$ G) was observed by EPR spectroscopy from reacting $\text{PPN}[\text{Rh}(\text{CO})_4]$ with 3,4-dichloronitrobenzene by S. Cenini *et al.* While the structure was unknown at that time, we believe that the radical is similar to the unsymmetrical radical observed by us. This type of radical was proposed to be a key intermediate in the reductive carbonylation of aromatic nitro compounds.⁷

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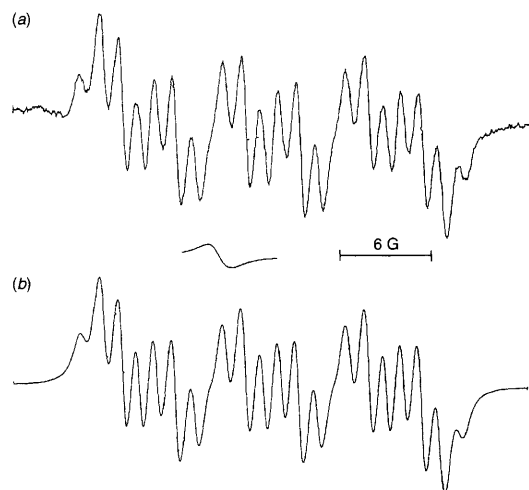


Fig. 2 EPR spectra from the reaction of 4-chloronitrobenzene with $\text{PPN}[\text{Rh}(\text{}^{13}\text{CO})_4]$ (a) under the conditions used in Fig. 1(b) and (b) a simulation spectrum of the radical observed in (a) using the parameters 8.84 ($I = 1, 1$), 3.88 ($I = 1/2, 1$), 1.35 ($I = 1/2, 2$), 1.56 ($I = 1/2, 1$) and 0.95 G ($I = 1/2, 1$)