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Bis(benzene)chromium. A Sandwich Complex Spin Trap As Revealed by ENDOR Spectroscopy

E. Samuel,[*,†] D. Caurant,[†] D. Gourier,[†] Ch. Elschenbroich,[‡] and K. Agbaria[‡]

Contribution from the Ecole Nationale Supérieure de Chimie de Paris (UMR 7576 and 7574 CNRS), 11 rue P. et M. Curie, 75231 Paris Cedex 05, France, and Fachbereich Chemie, Philipps-Universität, D-35032 Marburg, Germany

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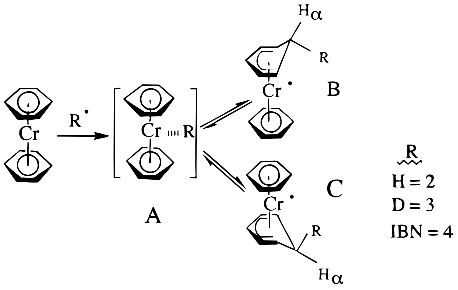
Abstract: Bis(benzene)chromium $[(\eta^6\text{-}C_6H_6)_2Cr]$ (BBC) is shown to readily trap radical species R (R = H, D, isobutyronitrile (IBN)) to form complex paramagnetic adducts whose structure has been identified in frozen solution by ENDOR (electron nuclear double resonance spectroscopy). It is shown that radical attack yields the 17 valence electron species $(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_6R)Cr$ where R assumes the *endo* position of the η^5-ring with respect to the metal in a dynamic interannular migration mediated by the central metal atom. It is further shown that $PhSiH_3$ (Ph = phenyl) is an efficient source of hydrogen atoms in the presence of BBC as well as other conventional nitroxide spin traps.

Introduction

The reactivity of organic radicals toward metal sandwich compounds is of utmost interest in the understanding of organometallic reaction mechanisms, stereochemistry, and electron-transfer pathways.[1] Yet, precedents for such reactions are very limited. The only well-documented example is radical ($R^\bullet$) addition to 19 valence electron (VE) cobaltocene to give the 18 VE neutral complex $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_5R)Co$.[2] As has been shown by $\{^1H\}$ NMR, in this adduct the group R is bound to an sp^3 carbon atom of the η^4 ring in an *exo* position with respect to the central cobalt atom. Radical addition to bis(arene)metal complexes, to our knowledge, has never been observed.[3] Here we report on the facile addition of radicals to bis(benzene)chromium **1** to give the 17 VE species $(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_6R)Cr$ (R = H (**2**), D (**3**), isobutyronitrile (IBN) (**4**)), Scheme 1.

Radical addition to **1** occurs under the same conditions as those used in the conventional spin trapping reactions where the respective spin adducts exhibit characteristic EPR spectra of the paramagnetic species formed. This observation leads to the surprising conclusion that bis(benzene)chromium is an efficient organometallic spin scavenger. However, due to the particular nature of the spin adduct produced which will be described below, EPR was not of sufficient resolution for the study. We therefore used ENDOR spectroscopy which allowed us to provide evidence as to the nature and configuration of the species formed.

Scheme 1



Experimental Section

All experiments were conducted under argon on saturated solutions of **1** in toluene (about 10^{-2} M). In each experiment, the solution was heated to 40 °C for a few minutes to eliminate all traces of the paramagnetic cation $\mathbf{1}^{\bullet+}$ inadvertently present, brought back to room temperature, and checked to be EPR silent before introducing the radical generator. Photolysis was performed with a Hanau low-pressure mercury vapor lamp. EPR spectra were recorded with a Bruker 220 D X-band spectrometer equipped with a standard TE_{102} cavity and a variable temperature accessory for temperatures in the range 100 K < T < 300 K and with an Oxford Instruments EPR continuous-flow helium cryostat for 20 K < T < 100 K. ENDOR experiments were performed in deuteriotoluene in order to avoid hyperfine interactions with solvent protons. A Bruker cavity was used working in the TM_{110} mode with a 100-W ENI broad-band power amplifier. Spectra were detected using frequency modulation of the rf carrier at a frequency of 12.5 kHz. With this modulation scheme, the ENDOR signal has the shape of the first derivative of the ENDOR enhancement.

Radical Sources and Reaction Procedures

1. $PhSiH_3$ and $PhSiD_3$. In the course of this investigation we discovered that phenylsilane and deuteriophenylsilane can be used as convenient sources of ^1H and ^2H radicals, a result which does not seem to have been reported eariler.[4] Thus,

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[†] Ecole Nationale Supérieure de Chimie de Paris.

[‡] Philipps-Universität.

(1) Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier: Amsterdam, The Netherlands (*J. Organomet. Chem. Library* **1990**, 22).

(2) Herberich, G. E.; Schwarzer, J. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 897.

(3) The reaction of the 20 VE complex bis(hexamethylbenzene)iron, $(HMB)_2Fe^0$, with organic halides RX may proceed through initial electron transfer to yield $[(HMB)_2Fe(I), R^\bullet] + X^-$ followed by coupling (within the solvent cage) of $R^\bullet$ with the 19 VE radical cation $(HMB)_2Fe^{\bullet+}$: Madonik, A. M.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 2437. Intramolecular radical addition to the benzene ring of $(\eta^6\text{-arene})Cr(CO)_3$ has been observed fairly recently and employed in organic synthesis: Schmalz, H. G.; Siegel, S.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2383.

(4) See for example: (a) Perkins, M. J. *Adv. Phys. Org. Chem.* **1980**, *1*, 17. (b) Chandra, H.; Davidson, M. T.; Symons, M. C. R. *J. Chem. Soc., Faraday Trans.* **1983**, *79*, 2705. (c) Janzen, E. G.; Liu, I. *J. Magn. Reson.* **1973**, *9*, 510.

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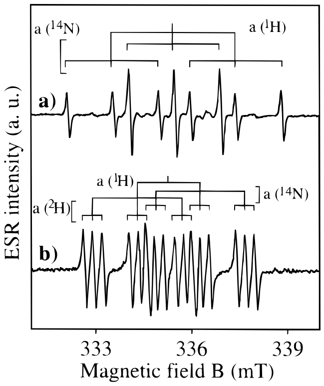

Figure 1. EPR spectrum at room temperature of a toluene solution containing (a) DMPO and $PhSiH_3$ photolyzed for 15 min (the spectrum is due to the DMPO/H spin adduct) and (b) the same solution with $PhSiD_3$ (the spectrum is due to DMPO/D spin adduct).

$PhSiH_3$ and $PhSiD_3$ were photolyzed for15 min in toluene and in the presence of a nitroxide spin trap, 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) or phenyl-*N*-*tert*-butylnitrone (PBN). In both cases EPR spectra of the characteristic nitroxide spin adducts were obtained.

Figure 1 shows the spectra observed with $PhSiH_3$/DMPO and $PhSiD_3$/DMPO, respectively. These spectra exhibit the typical hf (hyperfine) patterns resulting from coupling of the unpaired electron on the nitrone with one ^{14}N and two equivalent H nuclei of the DMPO adduct, ($a(^{14}N) = 1.42$ mT; $a(H) = 1.89$ mT); 1 G = 0.1 mT) (Figure 1a). This is confirmed by performing the same experiment with $PhSiD_3$. In this case the spectrum exhibits coupling with one (trapped) D atom, $a(D) = 0.23(6)$ mT, and one hydrogen atom of the nitrone, $a(H) = 1.89$ mT (Figure 1b). This proves that one H and one D atom have been generated, respectively, from these two silanes and trapped by DMPO.

Using PBN as spin trap, spectra consistent with the formation of H and D spin adducts were obtained with both silanes (hydrogen atom from $PhSiH_3$ trapped with PBN, $a(^{14}N) = 1.53$ mT, $a(^1H) = 0.73(2)$ mT; deuterium atom from $PhSiD_3$ trapped with PBN, $a(^{14}N) = 1.49$ mT, $a(^1H) = 0.731$ mT, $a(D) = 0.10(7)$ mT). The parameters of the hydrogen adducts with both spin traps fully agree with the literature data.[4c]

2. Azaisobutyronitrile (AIBN). This compound is known to release isobutyronitrile (IBN) radicals by thermal treatment in solution at 70 °C. Blank experiments were performed with the above two spin traps, and the corresponding spin adducts were similarly obtained as evidenced by their EPR spectra and parameters. Thus, with PBN the spectrum consisted of a triplet of doublets ($a(N) = 1.43(2)$ mT, $a(H) = 0.31$ mT), indicating that the IBN radical has been trapped. These parameters are consistent with literature data on carbon-centered radicals trapped with PBN.[4b]

3. Reactions of I with H and D Radical Sources. $PhSiH_3$ and $PhSiD_3$ were added to solutions of **1** in toluene (see above) (**1**/silanes, 1:50 molar proportions) at room temperature and were stirred while heating to 40 °C for 15 min. Control by EPR revealed the formation of **2** and **3** with their spectra at their maximum intensity. Spectra of low intensity belonging to these two adducts were observed even at room temperature before heat treatment. These latter signals could also be enhanced by photolysis (for 20 min) to reach a maximum intensity equivalent with that observed by thermal treatment. The yields of **2** and **3** amount to about 15−20% referred to **1** initially present. This is concluded from a comparison with the spectral intensity obtained if an equivalent amount of **1** is subjected to oxidation to give $\mathbf{1}^+$. The latter reaction was independently controlled with a calibrated sample of dpph (diphenylpicrylhydrazyl) and was found to be almost quantitative.

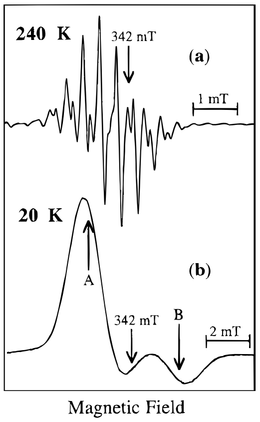

Figure 2. (a) Liquid and (b) frozen solution EPR spectra of the radical adducts (**2**, **3**, and **4**). Arrows A and B indicate the field settings used for ENDOR. Experimental parameters of the frozen solution spectrum: microwave frequency 9520 MHz; microwave power 0.2 mW; modulation amplitude 0.1 mT.

4. Reaction of 1 with AIBN. **1** was made to react with AIBN in toluene (**1**/AIBN, 1:3 molar proportions). Heating the mixture to 70 °C while stirring gave **4**, checked by EPR in the same manner as above. The maximum spectrum intensity reached was also similar.

Radical Trapping by 1

Generation of radicals from an appropriate source (see above) in the presence of **1** immediately gives in liquid solution a strong and highly structured isotropic EPR signal, best resolved at −40 °C, depicted in Figure 2. This spectrum, however, has the particularity of exhibiting a unique hyperfine pattern irrespective of the nature of the radical introduced. Both in liquid and in frozen solution (20 K), the spectrum is identical with that obtained previously by the reaction of a strong base $\mathbf{B}^-$ with the radical cation $\mathbf{1}^+$ and which was thought to lead to the deprotonated form of $\mathbf{1}^+$.[5] It was originally analyzed as an octet (coupling constant 0.39 mT) of triplets (0.635 mT). The unusual intensity ratio 1:4:1 of the triplets suggested that an alternating line width effect is operating, caused by a dynamic process in which two pairs of protons exchange their coupling constants (0.39 and 0.245 mT, respectively) in the frequency of intramolecular interannular proton exchange.[6] This amounts to the interaction of the unpaired electron on chromium with a total of 10 protons on the carbon atoms of the two rings, and one proton oscillating between the two sites on opposite rings of the sandwich structure, via the metal, at a rate on the order of 10^7 s^{-1} as deduced by simulation.[5] The frozen solution spectra of **2**, **3**, and **4** exhibit pseudoaxial line shapes with $g_{\|} = 1.975$ and $g_{\perp} = 1.999$, in striking contrast with the parameters and line shape of the spectrum of the radical cation $\mathbf{1}^{\bullet+}$ ($g_{\|} = 2.002$ and $g_{\perp} = 1.978$).[5] The conspicuous difference between these two spectra is the inversion of the g factor components. The rather unexpected identity of the hyperfine patterns and parameters of **2**, **3**, **4**, and the compounds produced by addition of $\mathbf{B}^-$ on $\mathbf{1}^+$ was the reason which led us to use ENDOR spectroscopy because of its higher resolving power as mentioned earlier.

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[5] Elschenbroich, Ch.; Gerson, F.; Heinzer, J. *Z. Naturforsch.* **1972**, *27b*, 312.

[6] Sullivan, P. D.; Bolton, J. R. *Adv. Magn. Reson.* **1970**, *4*, 39.

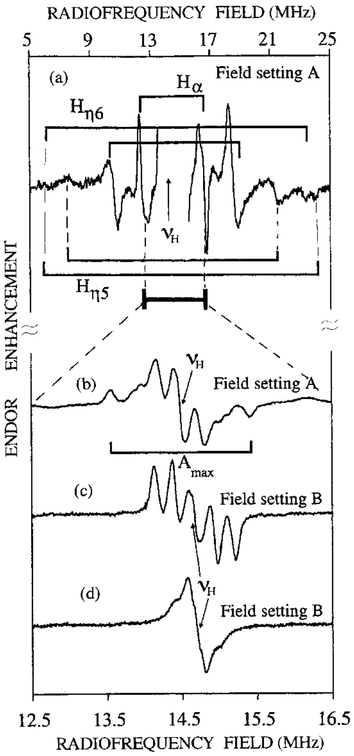

Figure 3. (a) ENDOR spectrum at 20 K of **2** (exactly the same spectrum is obtained for **3** and **4**). H_{η^6}, H_{η^5}, and H_α sets of lines indicate the principal hyperfine interaction with ring protons. (b), (c), and (d) are expanded views of the central region of the ENDOR spectrum: **4** (b, c), **3** (d). Microwave power 0.2 mW; radio frequency power 100 W; modulation frequency 12.5 kHz; modulation depth 100 kHz (a) and 40 kHz (b−d).

Figure 3a shows the proton ENDOR trace of **2**, recorded at the field setting **A** of the frozen solution EPR spectrum, Figure 2. It is composed of a strong line centered at the proton frequency ν_H, flanked by a series of doublets, more or less resolved, caused by hf interactions with nonequivalent protons of the molecule. The outermost broad and poorly resolved features labeled H_{η^6} and H_{η^5} represent the powderlike ENDOR lines of the η^6-benzene and the η^5-cyclohexadienyl ligands (Scheme 1). This part of the spectrum is independent of the nature of the attacking radical, as opposed to the central line and the inner doublet labeled H_α.

Despite the very low resolution of the H_{η^6} and H_{η^5} lines, the corresponding hf parameters were measured by studying the dependence of the ENDOR lines of **2**, **3**, and **4** on magnetic field and temperature, and also that of the symmetrical cation $\mathbf{1}^+$, which exhibits only H_{η^6} lines. Frozen solution spectra of paramagnetic sandwich compounds always exhibit ENDOR lines with a typical powder line shape at very low temperatures where all the molecular motions are frozen, and ENDOR lines with a single-crystal type line shape at temperatures where fast ring reorientation around the molecular axis partially averages the proton hf interaction.[7]

The temperature dependence of the frozen solution ENDOR spectrum of $\mathbf{1}^+$ gives an anisotropic hf tensor for η^6-benzene hydrogen nuclei with $A_1 = 7.0(1)$ MHz, $A_2 = 5.8(6)$ MHz, $A_3 = 16.0(0)$ MHz, and $A_{iso} = 9.6(5)$ MHz. Returning to the spectra of **2**, **3**, and **4**, the complexity and the poor resolution of the low-temperature spectrum in Figure 3 indicates a low symmetry for these compounds affected by radical addition. At 20 K ring reorientation as well as interannular group exchange (Scheme 1) are frozen, so that all the hydrogen atoms of **2**, **3**, and **4** are pairwise inequivalent. The η^6-benzene hydrogen lines H_{η^6} were, however, identified by the fact that upon increasing the temperature from 20 to 100 K, these lines merge into two lines with single-crystal type line shape (i.e., symmetrical line shape) brought about by the η^6-benzene reorientation around the molecular axis. The hf tensor of η^6-benzene protons was found to be $A_1 \cong A_2 \cong 7.3(8)$ MHz, $A_3 \cong 17.7(8)$ MHz, and $A_{iso} \cong 10.8(4)$ MHz. These values are slightly larger than the hf parameters of η^6-benzene protons of $\mathbf{1}^+$. The poorly resolved ENDOR features of **2**, **3**, and **4** labeled H_{η^5} are due to the protons of the η^5-cyclohexadienyl ligand to which the radical is attached (Scheme 1). This ligand does not exhibit reorientational motion upon increasing the temperature, so that these parameters cannot be measured accurately. However, from the position of the H_{η^5} features, the hf tensor of the η^5-cyclohexadienyl hydrogen nuclei can be roughly estimated to be $A_1 \cong A_2 \cong 12.(6)$ MHz, $A_3 \cong 19.(4)$ MHz, and $A_{iso} \cong 14.(9)$ MHz.

The narrow and almost symmetrical single-crystal-like inner doublet labeled H_α in **2**, **3**, and **4**, Figure 3a, is due to the quasi isotropic hf interaction with the hydrogen atom at the α position of the molecule (Scheme 1). We have verified that the shape and the splitting mode of this doublet are independent of the field setting value. This shows that the anisotropic part of the H_α hf tensors is very small, a feature which indicates that the purely dipole−dipole interaction (which is positive) is nearly compensated by a negative interaction due to an unpaired spin density at the adjacent carbon atom. It should be emphasized that the ENDOR spectrum of **4** is identical to that of **2** and **3** except for the following features: (i) the hf coupling to H_α equals 3.54 MHz in **4** and 4.14 MHz in **2** and **3**. This difference indicates that the nearest neighbors of these H_α protons are different because of the nature of the attacking radicals and (ii) the structure of the central line of **4** is also very different from that of **2** and **3**, Figure 3b−d. In the case of **2** and **3** the central signal is reduced to a narrow line at the proton frequency ν_H and without clearly resolved features, Figure 3d. This line is due to the hf interaction with residual protons of solvent cage molecules. In the case of **4**, Figure 3b,c, the central region exhibits a complex, well-resolved structure with two or three doublets, depending on the field setting. These additional lines must be attributed to hf interactions with protons H_γ belonging to the IBN substituent located at the η^5-cyclohexadienyl ring, Scheme 1. This striking difference between the spectra of **2** and **3** and that of **4** must be attributed to the nature of the attacking radical.

To sum up, all the radical adducts **2**, **3**, and **4** have in common rigorously the same liquid and frozen solution EPR spectra and the same local ENDOR spectra for the η^5 and η^6 protons. They only differ by the values of the hf interactions of their individual H_α protons and by the identification of the trapped IBN radical, both resolved by ENDOR only. It can be asked at this juncture why then ENDOR fails to reveal a distinctive feature of the trapped H (and D) atoms also. As will be shown below, this feature most probably arises from the peculiar bonding characteristics of these trapped atoms and the problems inherent to their detection.

The question which remains to be addressed concerns the site of attachment (*endo* vs *exo*) of the attacking radical. The *endo* position is by far the more likely on the basis of the following features of the ENDOR spectrum. Parts b and c of

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[7] For measuring techniques of the proton hyperfine parameters, see: (a) Gourier, D.; Samuel, E. *J. Am. Chem. Soc.* **1987**, *109*, 4571. (b) Gourier, D.; Samuel, E.; Bochmann, B.; Hahn, F.; Heck, J. *Inorg. Chem.* **1992**, *31*, 86.

Figure 3 show that the magnitude of the hf interaction with the protons of the trapped IBN radical is dependent on the field setting chosen for microwave saturation. Field setting **A** corresponds to a selection of molecules oriented such that their axes (passing through the centers of the two rings) are perpendicular to the magnetic field. It is precisely at this molecular orientation that the hf interaction with the IBN protons (matrix line) is at its maximum ($A_{\max} = 1.88$ MHz, Figure 3b). Owing to the essentially dipolar nature of this hf interaction, the following equation applies:

$$A(\theta) = g\beta g_n\beta_n(3\cos^2\theta - 1)d^{-3}h^{-1}$$

where θ is the angle between the magnetic field and the Cr−H_γ connecting axis and d is the Cr−H_γ distance. $A_{\max}$ arises from the orientation $\theta = 0°$. Since $A_{\max}$ is encountered when the magnetic field is almost perpendicular to the molecular axis, this can only be accommodated with the radical R assuming the *endo* position. From the experimental value of $A_{\max}$, d is estimated to be 4.4 Å in fair agreement with a molecular model of **4**.

Discussion

It is clear from the above that Scheme 1 accounts for the experimental observations and shows why EPR and ENDOR are requisite complementary techniques to interpret the phenomena under study. Whereas EPR merely indicates that an interannular dynamic effect is operating yet fails to provide further information on the geometry of the static configurations, ENDOR supplies the magnitudes of hf interaction parameters pertaining to H_α and R protons (R = IBN) which turned out to be different and too small to be measured by EPR. ENDOR therefore differentiates between the products arising from the attack of different radicals on **1**.

The identity of the EPR spectra obtained from the reactions of **1** + R (this paper) and $\mathbf{1}^+ + \mathbf{B}^-$ [5] suggests that in the latter case the addition proceeds by the formation of the neutral species **1** as a first step, followed by the capture of a H atom generated from protic impurities adventitiously present.[8] Therefore, capture of a hydrogen radical by **1** rather than deprotonation of $\mathbf{1}^+$ probably had occurred in the reactions described in ref 5. Alternatively, radicals for subsequent attack at **1** could also be formed in an initial electron-transfer step $\mathbf{B}^- + \mathbf{1}^+$ to give $\mathbf{B}^\bullet +$ **1**, considering the fact that most of the bases $\mathbf{B}^-$ employed in ref 5 are also strong reducing agents.

Radical addition to an arene represents the first step in homolytic aromatic substitution, a process which is plagued by low reactivity and selectivity.[9] Therefore, it does not come as a surprise that radical addition to the solvent toluene does not appear to compete with radical addition to the metal complex **1**. The latter contains benzene rings which bear a negative partial charge,[10] and which therefore should exhibit an increased susceptibility to attack by an electrophilic radical such as IBN. Stereospecific *endo* addition to η-benzene in **1** can be explained by primary attack of the radical at the central metal atom which is followed by transfer of the radical to one of the coordinated rings, with concomitant metal-to-ligand electron transfer generating an η^5-cylohexadienyl system. The newly formed C−C bond should experience an agostic interaction with the central metal, thereby becoming weaker. The scene is set, then, for reversible intramolecular interannular transfer of the group R (forms **B** and **C**, Scheme 1) via the transition state **A** which is the dynamic process required to account for an alternating line width effect in the isotropic EPR spectra of the radical adducts **2**, **3**, and **4**. *Endo* addition of the radical to **1** is corroborated by the finding that upon heating the probe which contains the paramagnetic species **B** and **C**, to 120 °C, the EPR spectrum vanishes, and the residue contains unsubstituted **1** only. Therefore, thermal cleavage of the C(arene)−R bond rather than that of the C(arene)−H_α bond occurs, the former bond being labilized by interaction with the central metal atom. This presupposes that, in **B** and **C**, the C(arene)−metal bond assumes an *endo* orientation. The ease of this back reaction explains why attempts to isolate the radical adducts from **1** on a preparative scale have failed as yet.

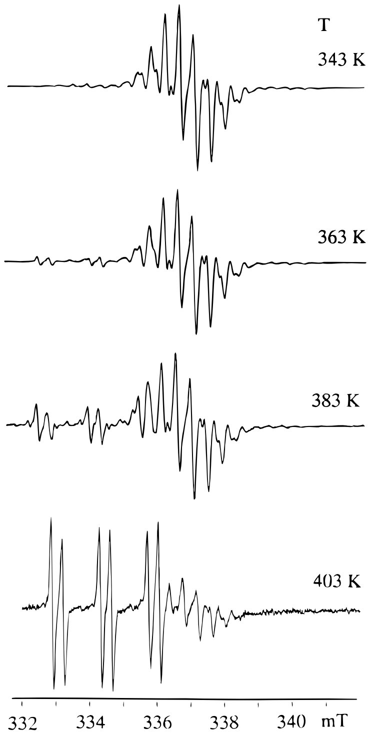

Figure 4. Experiment illustrating competition of spin trapping using simultaneously BBC and AIBN in the presence of PBN in toluene. At room temperature only BBC−IBN spin adduct **4** is formed. Increasing the temperature, IBN radical is transferred to PBN to form PBN−IBN spin adduct.

Since in this back reaction the leaving group is identical with the originally entering one, radical addition to **1** fails to constitute the first step in homolytic substitution at **1**. Furthermore, because of its *endo* position, the trapped hydrogen atom becomes prone to weak interactions with the C and the metal atoms and hence more sensitive to intermolecular (complex solvent) interactions. Consequently, the distribution of this interaction inherent to the frozen solution should result in a distribution of C−H⋯Cr distances, and should thus induce a distribution of the corresponding hydrogen hf parameters. This would explain why ENDOR lines of the trapped hydrogen (deuterium) atom are broadened beyond recognition.

The astonishingly high trapping potential of **1** has been further demonstrated by competition experiments: IBN radicals were generated in the presence of equimolar amounts of **1** and PBN spin trap. As shown in Figure 4, at 70 °C exclusive formation of **4** is observed. After the EPR signal due to **4** had reached its

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(8) Compare the formation of (η^5-C_5H_5)(η^7-C_7H_8)Cr from (η^5-C_5H_5)(η^7-C_7H_7)Cr: Elschenbroich, Ch.; Gerson, F.; Stohler, F. *J. Am. Chem. Soc.* **1973**, *95*, 6956.

(9) Fossey, J.; Lefort, D.; Sorba, J. *Free Radicals in Organic Chemistry*; Wiley: Chichester, England, 1995; Chapter 14.

(10) Binder, H.; Elschenbroich, Ch. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 659.

maximum intensity, gradually raising the temperature to 130 °C led to a decrease in the concentration of **4** and the appearance of the EPR signal of the spin adduct PBN−IBN. The magnitudes of the coupling constants demonstrate that BBC−IBN (**4**) transfers the group IBN rather than a hydrogen atom to PBN.[4b] Clearly, **4** represents the kinetically controlled spin adduct, and **1** therefore may serve as a convenient storage medium for radicals to be employed in subsequent conversions. In light of these results it is not unlikely that **1** should exhibit hitherto unknown properties such as radical-promoted reactions with organic substrates. Finally, the dynamic process depicted in Scheme 1 is a novel feature of one of the archetypical molecules of organometallic chemistry.

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