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Short communication

Charge transfer interaction between bis(triphenylphosphine)copper(I) borohydride and 9,10-phenanthrenequinone. Absorption spectrum and photoreactivity of the donor–acceptor adduct

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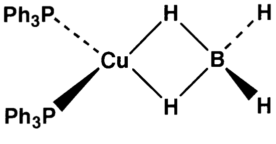
Abstract

The complex $(PPh_3)_2CuBH_4$ and 9,10-phenanthrenequinone form a weak adduct in CH_2Cl_2 which dissociates into its components in DMSO. The adduct is characterized by $(PPh_3)_2CuBH_4 \rightarrow$ phenanthrenequinone outer sphere charge transfer (OSCT) absorptions at $\lambda_{max} = 707$ and 514 nm. The coordinated $BH_4{}^-$ ligand reduces the quinone to hydroquinone thermally and photochemically by OSCT excitation with $\phi = 0.05$ at $\lambda_{irr} = 700$ nm. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Electronic spectra; Charge transfer; Copper complexes; Borohydrides; Quinones

1. Introduction

Borohydrides (or boranates) such as $BH_4{}^-$ are versatile hydridic reductants in inorganic and organic synthesis. Recently, it has been shown that borohydrides can also be used as photoreductants [1,2]. In these cases, boranate anions and oxidizing cations form ion pairs which are characterized by outer sphere charge transfer (OSCT) absorptions. OSCT excitation leads to the reduction of the cation and oxidation of the boranate. This redox process may proceed as a hydride transfer [2]. Moreover, borohydrides are important ligands in transition metal complexes [3–6]. Although the reducing strength of borohydrides is attenuated by coordination, such metal complexes are still valuable reductants. In this context, it is of interest if coordinated boranates can also function as OSCT donors and photoreduce organic substrates. We explored this possibility and selected the complex $(PPh_3)_2Cu^IBH_4$ as donor for the present study.



This choice was based on the following considerations. The complex $(PPh_3)_2Cu^IBH_4$ is rather stable [7] and its excited state properties are well-known [8–10]. This compound is commercially available (Aldrich) as a selective reductant in organic synthesis, in particular for the reduction of carbonyl compounds [11,12]. In addition, $(PPh_3)_2CuBH_4$ has been reported to reversibly form weak adducts with aldehydes and ketones although the nature of these addition compounds does not seem to be clear [12]. As CT acceptor for $(PPh_3)_2CuBH_4$, we chose 9,10-phenanthrenequinone as a promising candidate since it has been previously shown to undergo an OSCT interaction with Cp_2MH_2 (Cp = cyclo—pentadienyl and M = Mo, W) as hydridic donors [13,14].

2. Experimental

2.1. Materials

All solvents used were of spectrograde quality. The compounds $(PPh_3)_2CuBH_4$, $(PPh_3)_3CuCl$, $Na[BH_3CN]$ and 9,10-phenanthrenequinone were commercially available (Aldrich) and used without further purification.

2.2. Instrumentation

Absorption spectra were measured with a Hewlett Packard 8452A diode array or an Uvikon 860 absorption

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spectrometer. The light source used was an Osram HBO 200 W/2 or an Osram XBO 450 W/4 lamp. Additional cut-off filters (Schott) were applied to avoid short-wavelength and second-order photolysis. Monochromatic light was obtained using a Schoeffel GM/1 high-intensity monochromator (band width = 23 nm). In all the cases, the light beam was focused on a thermostated photolysis cell by a quartz lens. Emission and excitation spectra were recorded on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier for measurements up to 900 nm. The luminescence spectra were corrected for monochromator and photomultiplier efficiency variations.

2.3. Photolyses

The photolyses were carried out in solutions of CH_2Cl_2 and $CHCl_3$ in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV–visible spectrophotometry. For quantum yield determinations, the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by ferrioxalate actinometry and equipped with a RkP-345 detector.

3. Results

Yellow solutions of 9,10-phenanthrenequinone in CH_2Cl_2 show absorptions (Fig. 1) at $\lambda_{max} = 418$ ($\varepsilon = 1400\,dm^3\,M^{-1}\,cm^{-1}$), 329 (2400) and 210 (23000) nm. This spectrum is hardly solvent dependent. Upon addition of colorless $(PPh_3)_2CuBH_4$, a homogeneous solution is formed. The yellow color of this solution slowly changes to reddish-grey. The concomitant spectral variations (Fig. 1) indicate the formation of a new species with the longest wavelength absorption at $\lambda_{max} = 707$ nm. Upon addition of rather polar solvents such as dimethylsulfoxide the original spectrum of phenanthrenequinone is completely restored. It is assumed that the new species is a weak adduct between $(PPh_3)_2CuBH_4$ and phenanthrenequinone. This assumption is supported by the observation that the absorption spectrum of phenanthrenequinone is still preserved in the spectrum of the adduct. The difference spectrum of the new species and phenanthrenequinone (Fig. 2) yields absorptions at $\lambda_{max} = 707$ and 514 nm which are attributed to CT interactions in the adduct. While $(PPh_3)_2CuBH_4$ is luminescent [9–11] ($\lambda_{max} = 475$ nm), neither phenanthrenequinone nor the adduct show an emission. The adduct in CH_2Cl_2 is not stable but undergoes an irreversible reaction. Owing to the interference by this secondary reaction, reliable extinction coefficients of the CT absorptions and the stability constant of the adduct could not be determined. After several hours, the adduct completely decomposed as indicated by the disappearance of its absorption spectrum. Since $(PPh_3)_2CuBH_4$ is a well known reductant for organic carbonyl compounds [11,12], it was suspected that the irreversible reaction of the adduct leads to the reduction of phenanthrenequinone. Indeed, the formation of 9,10-phenanthrenediol was confirmed by the appearance of its characteristic fluorescence at $\lambda_{max} = 418$ nm [14]. While the thermal decomposition of the adduct is rather slow, it rapidly proceeds as photolysis by irradiation with white but also with red light. The disappearance of the adduct was monitored by measuring the decrease in the optical density at 707 nm. The adduct disappears with $\phi = 0.05$ at $\lambda_{irr} = 700$ nm.

For comparison, $Na^+BH_3CN^-$ and $(PPh_3)_3CuCl$ were also added to solutions of phenanthrenequinone. While BH_3CN^- immediately reduces phenanthrenequinone to the hydroquinone, $(PPh_3)_3CuCl$ and phenanthrenequinone do not undergo any interactions as indicated by the invariance of the absorption spectrum.

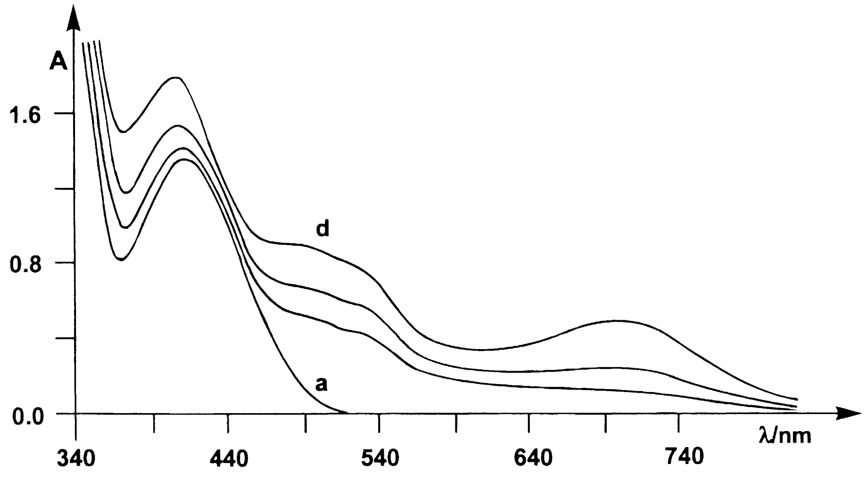

Fig. 1. Electronic absorption spectrum of 9.64×10^{-4} M phenanthrenequinone in CH_2Cl_2 at room temperature (a) and the mixture of this solution with $(PPh_3)_2CuBH_4$ (2.0×10^{-3} M) after 10, 20 and 40 min (d) standing in the dark (1 cm cell).

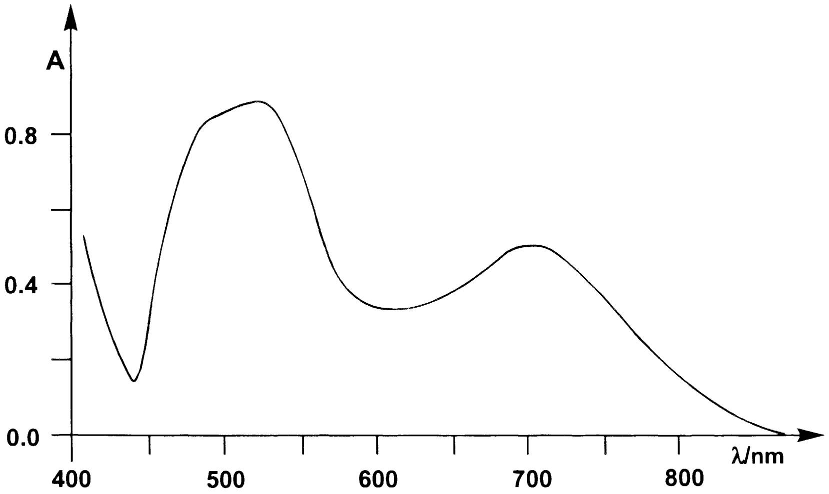

Fig. 2. Difference in absorption spectrum between a mixture of 9.62×10^{-4} M phenanthrenequinone and 2.0×10^{-3} M $(PPh_3)_2CuBH_4$ in CH_2Cl_2 after 40 min standing in the dark and 9.62×10^{-4} M phenanthrenequinone in CH_2Cl_2 at RT (1 cm cell).

4. Discussion

It is suggested that the initial reaction of $(PPh_3)_2CuBH_4$ and 9,10-phenanthrenequinone leads to the formation of an adduct $[(PPh_3)_2CuBH_4 \times$ phenanthrenequinone] which is characterized by $(PPh_3)_2CuBH_4 \rightarrow$ phenanthrenequinone OSCT absorptions at $\lambda_{max} = 707$ and 514 nm (Fig. 2). The addition compound $[Cp_2WH_2 \times$ phenanthrenequinone] shows a similar CT spectrum [13,14]. Generally, the formation of CT complexes is fast, but occasionally it proceeds rather slowly [15,16] as observed in the present work. The adduct $[Cp_2WH_2 \times$ phenanthrenequinone] as well as $[(PPh_3)_2CuBH_4 \times$ phenanthrenequinone] are not very stable. They undergo a facile dissociation into their components in polar solvents such as DMSO.

It is assumed that the CT donor function of $(PPh_3)_2Cu^IBH_4$ is based on the presence of the BH_4^- ligand since $(PPh_3)_3CuCl$ does not form a CT adduct and does not react with phenanthrenequinone. Moreover, the donor properties of borohydrides coordinated to Cu(I) are also documented by electrochemical studies [17] and by the fact that these complexes are versatile reducing agents [11,12]. Indeed, the formation of the CT adduct $[(PPh_3)_2CuBH_4 \times$ phenanthrenequinone] is followed by the irreversible reduction of phenanthrenequinone to the hydroquinone. The CT assignment of the long-wavelength absorption of $[(PPh_3)_2CuBH_4 \times$ phenanthrenequinone] is consistent with the photochemical behavior of the adduct. $(PPh_3)_2CuBH_4 \rightarrow$ phenanthrenequinone OSCT excitation leads also to the reduction of the quinone which may proceed as a hydrogen transfer from the coordinated BH_4^- ligand to the quinone.

A comparison of $[(PPh_3)_2CuBH_4 \times$ phenanthrenequinone] with other CT complexes of neutral transition metal complexes [18] is a further point of interest. For example, $[M^0(arene)(CO)_3]$ donors (M = Cr, Mo, W) form CT adducts with trinitrobenzene and tetracyanoethylene as acceptors [19–23]. In the case of $[Cr(anisol)(CO)_3]$ it has been shown that the CT interaction occurs by coplanar face-to-face orientation of trinitrobenzene to the coordinated arene [20,24]. Unfortunately, owing to its instability $[(PPh_3)_2CuBH_4 \times$ phenanthrenequinone] cannot be structurally characterized. However, it may be speculated that the CT interaction takes place by a direct contact between the coordinated BH_4^- ligand and phenanthrenequinone. This interaction could be mediated by some type of B–H... O=C< hydrogen bonding. Generally, hydrogen bonding is based on proton donation from very electronegative elements such as F, O and N and not from less electronegative elements such as boron. However, recent observations have revealed new types of hydrogen bonding involving also metal–hydride bonds [25,26].

Acknowledgements

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References

[1] H. Kunkely, A. Vogler, Collect. Czech. Chem. Commun. 66 (2001) 119.
[2] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 3 (2000) 624.
[3] C.E. Housecroft, T.P. Fehlner, Adv. Organomet. Chem. 21 (1982) 57.
[4] R.N. Grimes (Ed.), Metal Interactions with Boron Clusters, Plenum Press, New York, 1982.
[5] J.D. Kennedy, Progr. Inorg. Chem. 34 (1986) 211.
[6] C.E. Housecroft, Boranes and Metalloboranes, Ellis Horwood, New York, 1994.
[7] J.M. Davidson, Chem. Ind. London (1964) 2021.
[8] D.P. Segers, M.K. DeArmond, P.A. Grutsch, C. Kutal, Inorg. Chem. 23 (1984) 2874.

[9] B. Liaw, S.W. Orchard, C. Kutal, Inorg. Chem. 27 (1988) 1311.

[10] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.

[11] T.N. Sorrel, R.J. Spillane, Tetrahedron Lett. (1978) 2473.

[12] G.W.J. Fleet, P.J.C. Harding, Tetrahedron Lett. 22 (1981) 675, and references cited therein.

[13] A. Nakamura, S. Otsuka, Bull. Chem. Soc. Jpn. 49 (1976) 3641.

[14] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 1 (1998) 200.

[15] M.R. Mahmoud, M.M.A. Hamed, H.M.A. Salman, Spectrochim. Acta 44A (1988) 1185.

[16] M.R. Mahmoud, A.M. Al-Nady, A.A. Mohamad, H.M.A. Salman, Gazz. Chim. Ital. 119 (1989) 157.

[17] G.B. Jacobsen, J.H. Morris, D. Reed, J. Chem. Res. (1982) (S) 319; (M) 3601.

[18] A. Vogler, H. Kunkely, Top. Curr. Chem. 158 (1990) 1.

[19] I.W. Fitch, J.J. Lagowski, J. Organomet. Chem. 5 (1966) 480.

[20] G. Huttner, E.O. Fischer, R.D. Fischer, O.L. Carter, A.T. McPhail, G.A. Sim, J. Organomet. Chem. 6 (1966) 288.

[21] G. Huttner, E.O. Fischer, J. Organomet. Chem. 8 (1967) 299.

[22] H. Kobayashi, M. Kobayashi, Y. Kaizu, Bull. Chem. Soc. Jpn. 46 (1973) 3109.

[23] H. Kobayashi, M. Kobayashi, Y. Kaizu, Bull. Chem. Soc. Jpn. 48 (1975) 1222.

[24] O.L. Carter, A.T. McPhail, G.A. Sim, J. Chem. Soc. A (1966) 822.

[25] R.H. Crabtree, O. Eisenstein, G. Sini, E. Peric, J. Organomet. Chem. 567 (1998) 7.

[26] R.H. Crabtree, J. Organomet. Chem. 577 (1998) 111.