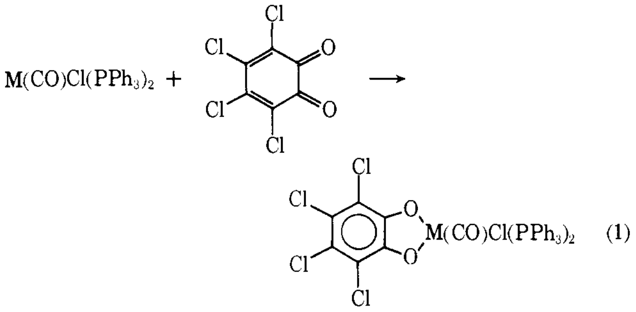
Thermal Oxidative Addition of *o*-Quinones to Low-Valent Metal Complexes

Sir:

The interactions of *p*-quinones with a number of transition metal complexes have been described. A number of complexes involving *p*-quinone ligands, which function as chelating diolefins, have been prepared.[1] *p*-Quinones have also been shown to form charge-transfer complexes with a number of transition metal compounds.[2] The oxidative addition of *p*-benzoquinone to $[Co(CN)_5]^{3-}$ has been reported to yield $[(CN)_5CoOC_6H_4OCo(CN)_5]^{6-}$.[3] In contrast, the formation of metal complexes of *o*-quinones has received much less attention. The detailed structures of the *o*-quinone adducts of some simple metal salts[4] and of the products of stoichiometry Ni(*o*-quinone)$_2$ which result from the oxidation of nickel carbonyl with various *o*-quinones[5] remain uncertain. Recently the photoinduced addition of 9,10-phenanthrenequinone and 1,2-naphthoquinone to $Ir(CO)Cl(PPh)_2$ has been reported.[6] Herein we report on the facile, *thermal* addition of *o*-quinones to several transition metal complexes.

The complexes $M(CO)Cl(PPh_3)_2$ (M = Ir, Rh) react rapidly in the absence of light with tetrachloro-1,2-benzoquinone to yield diamagnetic, nonelectrolytic adducts according to reaction 1.[7] The structure **1** is assigned to these adducts on the basis of the following information. (1) The strong carbonyl stretching absorption of the free quinone at 1711 and 1692 cm^{-1} (CH_2Cl_2 solution) is absent from the infrared spectra of the adducts **1a** and **1b**. Rather the infrared spectra of the adducts in the 1700–1400-cm^{-1} region appear as a superposition of absorptions due to triphenylphosphine and the tetrachloropyrocatecholate dianion. (2) The stretching frequencies of the coordinated carbon monoxide have increased from values of 1966 cm^{-1} (M = Ir) and 1981 cm^{-1} (M = Rh) in the parent complexes to 2062 cm^{-1} (M = Ir) and 2083 cm^{-1} (M = Rh) (all in CH_2Cl_2 solution) in the adducts. Such frequency increases are indicative of oxidation of the parent substrates.[8] As might be anticipated, this shift is greater for the adduct of tetrachloro-1,2-benzoquinone, **1a**, than that reported[6] for the adduct of the less electronegative 9,10-phenanthrenequinone. (3) *p*-Quinones such as 1,4-benzoquinone and tetrachloro-1,4-benzoquinone do not, under similar conditions, form adducts with parent complexes.



(1)

1a, M = Ir
b, M = Rh

The success of the thermal addition (reaction 1) is dependent on the oxidation potential[9] of the quinone. Strongly oxidizing quinones such as tetrachloro-1,2-benzoquinone and tetrabromo-1,2-benzoquinone readily add to $Ir(CO)Cl(PPh_3)_2$ in dichloromethane solution at 25°: the reaction appears to be completed upon mixing the reagents. Under similar conditions the weaker oxidants 1,2-naphthoquinone, 9,10-phenanthrenequinone, acenaphthenequinone, and benzil do not appear to form adducts, although the thermal addition of 9,10-phenanthrenequinone to this substrate has been reported to occur in refluxing benzene.[6]

Other d^8 complexes which are known to be susceptible to oxidative-addition reactions react thermally with tetrachloro-1,2-benzoquinone. Addition of this quinone to $(Ph_3P)_3RhCl$ produces green $(1,2\text{-}Cl_4C_6O_2)Rh(PPh_3)_2Cl$, **2**. The formation of **2** rather than $(1,2\text{-}Cl_4C_6O_2)Rh(PPh_3)_3Cl$ is probably due to steric effects. Treatment of solutions of **2** with various small bases caused the color to change to violet. In this way it has been possible to isolate violet $(1,2\text{-}Cl_4C_6O_2)Rh(PPh_3)_2Cl(\text{amine})$, where the amine is pyridine or *n*-propylamine. Reaction of the 1,5-cyclooctadiene complexes $[(1,5\text{-}C_8H_{12})MCl]_2$ (M = Rh, Ir) with tetrachloro-1,2-benzoquinone yields $[(1,2\text{-}Cl_4C_6O_2)M(1,5\text{-}C_8H_{12})Cl]_n$. The solubility of these last two complexes is so low that it has not been possible to determine their solution properties. The infrared spectra of all of these adducts indicate that the quinone is bound to the metal in a similar fashion to that found in **1**. Complexes of Pd(II) and Pt(II) such as $(Ph_3P)_2PdCl_2$, $(Ph_3P)_2PtCl_2$, and $(C_6H_6N)_2PdCl_2$, which are less susceptible to oxidative addition than are Rh(I) and Ir(I) complexes, do not form adducts with tetrachloro-1,2-benzoquinone.

The very reactive d^{10} complexes $(Ph_3P)_4Pt$ and $(Ph_3P)_3Pd$ react with tetrachloro-1,2-benzoquinone in dichloromethane solution to yield diamagnetic $(1,2\text{-}Cl_4C_6O_2)M(PPh_3)_2$. Similar thermal addition of 9,10-phenanthrenequinone to $(Ph_3P)_3Pt$ has been reported.[6] The infrared spectra of $(1,2\text{-}Cl_4C_6O_2)M(PPh_3)_2$ (M = Pt, Pd) resemble those of **1** except for the absence of bands due to metal–halogen and carbon monoxide vibrations.[10] The less reactive d^{10} complexes Ph$_3$-

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[1] For example: $(1,4\text{-}(CH_3)_4C_6O_2)Fe(CO)_3$, H. W. Sternberg, R. Markby, and J. Wender, *J. Amer. Chem. Soc.*, **80**, 1009 (1958); $(1,4\text{-}(CH_3)_4C_6O_2)Ni(\text{diolefin})$, G. N. Schrauzer and H. Thyret, *Chem. Ber.*, **96**, 1755 (1963); M. D. Glick and L. F. Dahl, *J. Organometal. Chem.*, **3**, 200 (1965); (*p*-quinone)$M(\pi\text{-}C_6H_5)$ (M = Co, Rh, Ir), G. N. Schrauzer and K. C. Dewhirst, *J. Amer. Chem. Soc.*, **86**, 3265 (1964); G. G. Aleksandrov, A. I. Gusev, V. S. Khandkarova, Yu. T. Strachkov, and S. P. Guben, *Chem. Commun.*, 748 (1969).

[2] A. S. Bailey, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc.*, 2579 (1965); B. Kamenar, C. K. Prout, and J. D. Wright, *ibid.*, 4851 (1965); C. K. Prout, R. J. P. Williams, and J. D. Wright, *ibid.*, 747 (1966).

[3] A. A. Vleck and J. Hauzlik, *Inorg. Chem.*, **6**, 2053 (1967).

[4] P. J. Crowley and H. M. Haendler, *ibid.*, **1**, 904 (1962), and references therein.

[5] F. Rohrscheid, A. L. Balch, and R. H. Holm, *ibid.*, **5**, 1542 (1966); G. N. Schrauzer and H. Thyret, *Z. Naturforsch. B*, **16**, 352 (1961).

[6] J. S. Valentine and D. Valentine, Jr., *J. Amer. Chem. Soc.*, **92**, 5795 (1970).

[7] *Anal.* Calcd for $(Cl_4C_6O_2)Ir(CO)Cl(PC_{18}H_{15})_2 \cdot CH_2Cl_2$: C, 47.6; H, 2.9; Cl, 22.4. Found: C, 48.1; H, 2.9; Cl, 22.8. Calcd for $(Cl_4C_6O_2)Rh(CO)(PC_{18}H_{15})_2 \cdot 1.5C_6H_{12}$: C, 58.7; H, 4.6; Cl, 16.7. Found: C, 58.6; H, 4.7; Cl, 16.6. The presence of solvent of crystallization has been verified by the ir and/or nmr spectra. Satisfactory analyses have been obtained for the other new complexes reported.

[8] L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

[9] The relative oxidation potentials of the quinones may be estimated from comparison of the polarographic half-wave potentials for their reduction: M. E. Peover, *J. Chem. Soc.*, 4540 (1962), and ref 5.

[10] The bonding in these complexes is clearly different from that

Ph_3PAuCl and Ph_3PAgCl do not form adducts with tetrachloro-1,2-benzoquinone.

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found in $(1,4\text{-}O_2C_6H_4)M(PPh_3)_2$ (M = Pd, Pt) and $(1,4\text{-}O_2C_{10}H_6)Pd(PPh_3)_2$: S. Takahashi and N. Hagihara, *J. Chem. Soc. Jap.*, **88**, 1306 (1967). In these complexes the *p*-quinones are undoubtedly coordinated through their olefinic portions[1] since $\nu_{C=O}$ suffers only a slight decrease of about 30 cm^{-1}. Their nmr spectra are also consistent with this mode of bonding.

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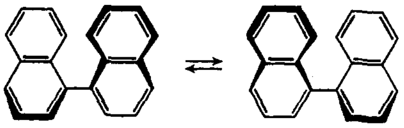
Solid State Resolution of Racemic 1,1'-Binaphthyl

Sir:

1,1'-Binaphthyl is a dissymmetric molecule and the rotation which interconverts enantiomers is only moderately hindered. The *S*-(+) form[1] has been obtained by resolution of the 4,4'-diamino derivative using α-bromo-π-camphorsulfonic acid followed by low-temperature deamination (through diazotization and hypophosphorous acid reduction).[2] (*S*)-(+)-1,1'-Binaphthyl has a half-life for racemization in solution of *ca.* 15 min at 50°.[2b,3]



S-(+) *R*-(−)

We report here that racemic binaphthyl may be resolved spontaneously into either of its optically active enantiomers simply by heating neat crystalline samples at 105–150°. Solid racemic binaphthyl can develop optical rotations as high as [α]D ±245° and subsequently be held at temperatures up to its melting point of 159° without loss of activity.[4] Three experimental approaches demonstrate the remarkable ability of binaphthyl to resolve in the absence of any external influence.

Partial resolution of 1,1'-binaphthyl occurs during solidification of melted samples. For example, ten samples of 20 mg each in sealed vials were totally immersed in a bath at 175° for several minutes in order to melt and destroy all seed crystals. The completely melted samples were transferred to a 150° bath and crystallization was induced by touching each sample vial with a piece of Dry Ice. After 20 hr at 150°, the samples were dissolved in benzene and the specific rotations obtained were [α]D −128, −17, +5, −76, −170, −124, −147, −115, +94, and −97° (benzene, 7 mg/ml). Other sets of samples gave similar scatterings of + and − rotations.[5]

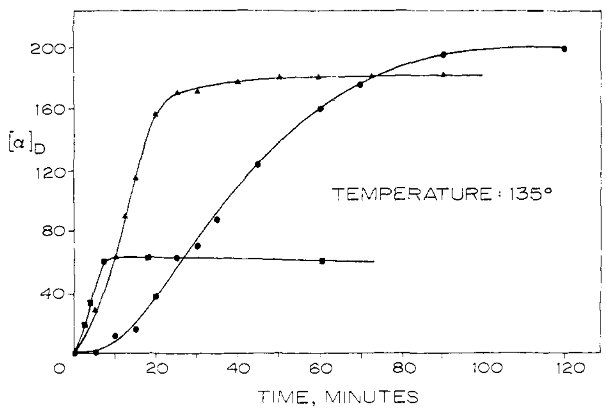


Figure 1. Development of optical activity in samples of neat, crystalline 1,1'-binaphthyl at 135°: ●, samples as crystallized from acetone;[8] ▲, same material ground into smaller crystals; ■, more finely ground samples. [α]D is the specific rotation of an individual sample dissolved in benzene for analysis of optical activity.

A second approach utilizing the polymorphic nature[6] of the (*R*,*S*)-binaphthyl system involves systematic enhancement of optical activity and produces larger quantities of highly resolved binaphthyl. Solid samples containing the low-melting form (mp 145°) were heated to 150°. At this temperature the racemic low form melts to a metastable liquid, which in turn crystallizes to the high melting (mp 159°) potentially[7] optically active form. An optical activity is produced which is at least as great as that of starting material. For example, binaphthyl with an initial rotation of [α]D 0.0° gave, after 2 hr at 150°, material with a specific rotation of +42°. Recrystallization from pentane is easily carried out so that there is no appreciable loss of optical activity. A crystalline mixture of racemic low-melting form and resolved high-melting form is obtained so that alternately recrystallizing from pentane between 35 and 0° and heating the neat solid to 150° for 2 hr boosted the rotation successively to +112, +186, and +194°. Initial use of + or − seed leads to production of the corresponding enantiomer.

The conversion of racemic solid binaphthyl to the optically active *S*-(+) or *R*(−) form is also possible at temperatures below 145° where liquid phase is less stable than any solid form, *i.e.*, the resolution occurs in the solid state. Figure 1 shows the development of optical rotation in a set of sealed neat samples of binaphthyl held at 135°. The binaphthyl used had [α]D +1.4° and was obtained by crystallization from acetone at −70° from a 0.056 *M* solution with initial activity of [α]D +9.4°.[8] X-Ray powder photographs

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(1) H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Lett.*, 97 (1968).

(2) (a) W. Theilacker and R. Hopp, *Chem. Ber.*, **92**, 2293 (1959); (b) A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 2365 (1963); A. K. Colter and L. M. Clemens, *J. Amer. Chem. Soc.*, 87, 847 (1965).

(3) A. K. Colter and L. M. Clemens, *J. Phys. Chem.*, 68, 651 (1964).

(4) This behavior is in contrast to that of *trans*-5-norbornene-2,3-dicarboxylic acid, which undergoes racemization in the solid state; R. E. Pincock, M.-M. Tong, and K. R. Wilson, *J. Amer. Chem. Soc.*, in press.

(5) The highest rotation at 5893 Å reported for samples of (+)-binaphthyl obtained by the classical resolution procedure is [α]D +192°.[2c] Cooke and Harris[2b] report [α] +245° at 5791 Å.

(6) Two crystalline forms of 1,1'-binaphthyl, with mp 145 and 159°, are known: Y. Badar, C. C. K. Ling, A. S. Cooke, and M. M. Harris, *J. Chem. Soc.*, 1543 (1965). The low-melting form is established as an *R,S* racemic compound: K. A. Kerr and J. M. Robertson, *ibid.*, *B*, 1146 (1969).

(7) From our results the high-melting form is a eutectic system of various amounts of (*R*)- and (*S*)-binaphthyl. If the sample produced were an equimolar mixture of *R* and *S* crystals it would be optically inactive. If, as is experimentally almost always the case, an excess of *R* (or *S*) crystals were produced the sample would be optically active.

(8) Samples of binaphthyl obtained by this procedure do not always develop high rotations in an orderly manner as illustrated in Figure 1. However, similarly seeded samples of binaphthyl develop some activity in the desired direction.