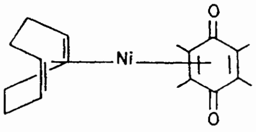
Low Temperature Protonation of Cyclo-octa-1,5-diene-(duroquinone)nickel(0)

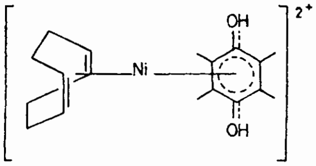
By Maurice Brookhart*
(*Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina* 27514)
and Glenda J. Young
(*East Tennessee State University, Johnson City, Tennessee* 37601)

Summary Cyclo-octa-1,5-diene(duroquinone)nickel(0) has been shown to protonate at the duroquinone carbonyls in HSO_3F to yield a stable dication. The chemical shift of the OH protons indicates very extensive positive charge delocalization through backbonding.

Extensive backbonding from nickel to duroquinone in diene(duroquinone)nickel(0) type complexes has been suggested to account for their high dipole moments and the shift of the carbonyl stretching frequency from 1629 cm^{-1} in free duroquinone to *ca.* 1550 cm^{-1} in the complexes.[1] We now report the results of low temperature protonation of the cyclo-octadiene(duroquinone)nickel complex, (I), which indicate that the basicity of the carbonyl oxygens of duroquinone has been very much enhanced as a result of this backbonding.



(I)



(II)

Extraction of a solution of (I) in CD_2Cl_2 into an HSO_3F–SO_2ClF solution (1 : 3/v : v) at −100° yielded a stable dark red solution of a new species thought to be the diprotonated complex (II). The ^1H n.m.r. spectrum† of (II) at −68° showed signals at δ 7·90 (2H, s, OH), 4·75 (4H, s, vinyl and an asymmetric band at δ2·65 (20H) assigned to the singlet for the four methyl groups (12H) superimposed on the broader methylene signal (8H). The assignment of the OH signal was substantiated by the fact that reversible line broadening could be observed at higher temperatures (*ca.* 15 Hz width at half height, −40°) as a result of rapid exchange of the OH protons with solvent acid.

The OH resonance has a very high field shift compared to other OH resonances of protonated carbonyl groups. The chemical shifts for these OH protons have been shown to be a good probe of positive charge delocalization and the normal range for such signals is *ca.* δ 12—15.[2-4] For comparison purposes the OH signal of diprotonated naphthoquinone occurs at δ 14·6.[2] The high field shift of the OH signals in (II) indicates that the basicity of the carbonyl groups in (I) has been enhanced through backbonding and that in the diprotonated species (II) there is extensive backbonding and positive charge delocalization to nickel.

The OH proton resonance is also observed as a narrow line in HSO_3F solution at −78°. Normally the OH signals of protonated carbonyl compounds and especially those of diprotonated species are not observed in HSO_3F solutions due to rapid exchange with solvent acid; the much more acidic HSO_3F–SbF_5 medium must be used sufficiently to increase the lifetime of the OH proton so that it may be observed by ^1H n.m.r.

(*Received, 5th November* 1973; *Com.* 1526.)

---

† All shifts relative to internal CH_2Cl_2 taken as δ 5·30. An upfield scan to δ −25 revealed no nickel hydride signal.

[1] G. N. Schrauzer, *Adv. Organometallic Chem.*, 1964, **2**, 26.
[2] M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 1735.
[3] T. Birchall and R. J. Gillespie, *Canad. J. Chem.*, 1965, **43**, 1045.
[4] G. A. Olah, D. H. O'Brien, and M. Calin, *J. Amer. Chem. Soc.*, 1967, **89**, 3582; G. A. Olah, and M. Calin, *ibid.*, 1968, **90**, 4672 and references therein.