Journal of Organometallic Chemistry, 253 (1983) C43—C46
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

NEAR-IR SPECTROSCOPIC STUDIES OF MIXED-VALENCE DI-, TRI-, AND TETRAFERROCENE DERIVATIVES

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(Received March 25th, 1983)

Summary

Near-IR data for a series of mixed-valence π-bond bridged and σ-bond bridged di-, tri-, and tetra-ferrocene derivatives suggests intervalence electron transfer (IT) exists in all of the π-bond bridged and some of the σ-bond bridged compounds. The compounds exhibiting the electron transfer transition include the mixed valence derivatives of 1,2-diferrocenylethene, 1,2-diferrocenyl-1,2-diphenylethene, azoferrocene, 1,1-diferrocenylethene, diferrocenyl ketone, ferricenyl(III)tris-ferrocenyl(II))borate zwitterion, triferrocenylphosphine oxide, diferrocenylphenylphosphine oxide and triferrocenylmethane. Compounds studied that do not exhibit the near-IR transition when oxidized are triferrocenylborane, triferrocenylphosphine, diferrocenylphenylphosphine and diferrocenylmethane. The near-IR transition in the π-bond bridged derivatives is attributed to a predominantly through-bond mechanism while the transition in the σ-bond bridged derivatives is attributed to a through-space mechanism. It is suggested that the presence of the IT band in the phosphine oxides while being absent in the phosphine derivatives may be due to a difference in the *dp*-π overlap of phosphorus and the cyclopentadiene rings in the two systems.

Some binuclear mixed-valence complexes exhibit a near-IR absorption band and there is evidence to suggest that this near-IR band is due to a mixed-valence electron transfer transition [1—6]. It has generally been accepted that the extent of metal—metal interaction in mixed-valence systems is mediated by the bridging group and that conjugation through a π-system is necessary for IT to occur. A recent study on the effect of bridging groups on IT in mixed valent biruthenium complexes has shown IT in systems where the bridging group is saturated [7].

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0022-328X/83/$03.00

Even here the interaction was attributed to coupling through the saturated bridge. We report here the study of a series of π-bond bridged biferrocene derivatives (II—VI) (Table 1) along with a series of σ-bond bridged di-, tri- and tetra-ferrocene derivatives (VII—XIII) (Table 1) in an effort to see what effect the bridging group has on the presence of the IT band. We would like to report the presence of an IT band in some saturated bridge compounds and suggest that here the interaction is not through the bridge but perhaps through space. Compounds II—XIII were prepared using published procedures. Monocations of the compounds were generated by controlled potential oxidation. Samples for absorption spectra were transferred from the electrolysis cell to a quartz flow cell and spectra were recorded within 20 minutes of sample preparation. Spectra were recorded at room temperature except for compounds IV—VI which were recorded at 5°C. Near-IR data for compounds I—XIII are reported in Table 1.

The monocations of all of the π-bridged compounds II—VI exhibit the new near-IR transition attributed to intervalence electron transfer. The energy and intensities of these bands are comparable to that of biferrocene (I) monocation 1800 nm (ϵ = 750) with the exception of diferrocenyl ketone (VI) where the band is at higher energy and much less intense 1280 nm (ϵ = 62). Of the σ-bond bridged compounds, only monocations VIII, X, XII, and XIII exhibit a new near-IR transition.

The band halfwidths $\Delta\bar{\nu}_{1/2}$ of the near-IR bands are consistent with the predictions of the Hush theory for weak interaction. The near-IR bands are sensitive to changes in solvents in compliance with the Hush dielectric continuum model, although no quantitative correlation with the solvent shifts was established. The

TABLE 1

NEAR-IR ABSORBTION DATA FOR MIXED VALENCE CATIONS

X	Mixed valence species formed from	λ_{max} (nm)	ϵ	$\Delta\bar{\nu}_{1/2}$ (cm^{-1})	α
I	Biferrocene [a]	1800	750	3600	0.09
II	1,2-Diferrocenylethene [a]	1750	1200	4300	0.09
III	1,2-Diferrocenyl-1,2-diphenylethene [a]	1740	1100	3800	0.08
IV	Azoferrocene [a]	1760	375	3700	0.05
V	1,1-Diferrocenylethene [a]	1800	200	3700	0.004
VI	Diferrocenylketone [a]	1280	62	3400	0.002
VII	Triferrocenylborane [b]	—	—	—	—
VIII	Ferricenyl(III)tris(ferrocenyl(II))-borate [b,d]	2200	300	—	—
IX	Triferrocenylphosphine [b]	—	—	—	—
X	Triferrocenylphosphine oxide [b]	1470	114	5000	0.003
XI	Diferrocenylphenylphosphine [b]	—	—	—	—
XII	Diferrocenylphenylphosphine oxide [b]	1160	64	—	—
XIII	Triferrocenylmethane [b]	1700	165	3750	0.004
XIV	Diferrocenylmethane	—	—	—	—
XV	[0.0]Ferrocenophane [e]	1550	2100	—	—
XVI	1,12-Dimethyl[1.1]ferrocenophane [f]	—	—	—	—
XVII	[1.1]Ferrocenophane [f,g]	750	3350	—	—
	Diferrocenylacetylene [a,c]	1560	670	5000	0.07
	1,4-Diferrocenylbutadiyne [a,c]	1180	570	5000	0.04

[a] In CH_2Cl_2 containing 0.2 *M* Bu_4NBF_4. [b] In CH_2Cl_2 containing 0.2 *M* Et_4NClO_4. [c] Ref. 8. [d] Ref. 9. [e] Ref. 12 and 13. [f] Ref. 12. [g] Ref. 12 suggests that "....perhaps this relatively intense band is the intervalence (IT) band for cation XVII."

interaction parameter (α) is the valence delocalization coefficient and can be estimated by:

$$\alpha^2 = \frac{4.5 \times 10^{-4}\ \epsilon_{\max} \Delta \bar{\nu}_{1/2}}{(\bar{\nu} r^2)}$$

where $\epsilon_{\max}$ is the molar absorbtivity, $\Delta\bar{\nu}_{1/2}$ is the band halfwidth, $\bar{\nu}$ is the absorption maximum and r is the donor-acceptor distance [2a]. α was calculated for the series of compounds and appears in Table 1. Of the compounds which show intervalence transfer, all belong to Class II under the classification defined by Robin and Day [10].

As all of the π-bond bridged mixed-valence compounds show the near-IR transition, and previously reported saturated bridged compounds (CH_2, Se, CH_2CH_2) [11] showed no near-IR transition, it was our initial postulate that π-bond bridging was a necessary condition for intervalence transfer to occur in these systems. The presence of an intervalence electronic transition in the ferricenyltris(ferrocenyl)borate zwitterion and now in the triferrocenylmethane cation prove this postulate incorrect as these compounds are σ-bond bridged. Comparing compounds XIII and XIV where the bridging groups are electronically similar, the IT band is seen in the more sterically crowded derivative. A similar comparison of compounds VIII and VII again reveals the presence of the IT band in the more crowded derivative. Here the bridging group in VIII might be expected to be even less conducive to through bond interaction as $p\pi$-$p\pi$ bond interaction would be expected to be greater in the tricovalent boron derivative than the tetracovalent BFc_4. These comparisons suggest that the IT band is not due to a through bond interaction in these cases but is due to direct exchange or a through space mechanism.

Also presented in the Table is near-IR data for the [0.0]- and [1.1]-ferrocenophanes XV and XVI. The dication of XVI has been shown to be diamagnetic [12] indicating direct metal—metal interaction in this species as superexchange through the saturated bridges is unlikely. There is also evidence for direct metal—metal interaction in the monocation of XV. A recent crystallographic study [14] shows the iron atoms shifted closer together in the monocation than they are in the neutral compound.

A working hypothesis at this time is to attribute the near-IR transition in σ-bond bridged mixed valence systems to IT via a through space mechanism, and in π-bond bridge systems to a through bond mechanism with through space interactions contributing when the metal centers are close enough to allow direct metal—metal interaction.

The presence of the IT band in the phosphine oxides while being absent in the phosphine derivatives provides an interesting dilemma. Using model compounds triphenylphosphine [15] and triphenylphosphine oxide [16], it is seen that the bond angles between the organic substituents are larger in the phosphine oxides than in the phosphines. This presents a situation different from the boron bridged (VII, VIII) or carbon bridged (XIII, XIV) systems where the IT band is observed in the more crowded derivatives. Although a through space mechanism cannot be excluded, it is tempting to speculate that the existence of the IT band in the phosphine oxide cations and absence of it in the phosphine cations is due to a difference in the *dp-π* overlap of phosphorus and the cyclopentadiene rings in the two systems.

We gratefully acknowledge partial support by the Solid State Chemistry Program, Division of Materials Research of the National Science Foundation (DMR80-15318).

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