VCD bands then the sign of these modes may be useful to fix the absolute configurations of approximately substituted analogues.

As a final note the mid-infrared VCD of (R)-α-phenylethyl-amine differs from that obtained as a dilute solution in carbon tetrachloride. The band at 1425 cm^{-1} (Figure 1) has positive VCD for (R)-1, which in carbon tetrachloride was reported[4] to be negative. This difference may be due to a product from the free radical reaction of the amine with carbon tetrachloride,[20] which quickly yields a number of products as well as a white precipitate.

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Remarkable Disruption of a Porphyrin. Insertion of a Ruthenium Atom into a Pyrrole Carbon–Nitrogen Bond of an N,N'-Vinyl-Bridged Porphyrin

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The complexation of metal ions by porphyrins (porphyrin metalation) has received considerable experimental study and invariably has led to the binding of metal ions to some or all of the pyrrole nitrogen atoms.[1] Recently we reported[2] that the N,N'-vinyl-bridged porphyrin 1[3] underwent an unusual series of

1, R = p-ClC$_6$H$_4$

metalations with metal carbonyls. In these reactions one or both of the N–C (vinyl) bonds were ruptured (Scheme I). Now we report the structural characterization of a second product resulting from the reaction of 1 with triruthenium dodecacarbonyl. In this case again C–N bond rupture occurs, but now it involves one of the pyrrole C–N bonds.[4]

Treatment of 1 with 2 mol of triruthenium dodecacarbonyl in boiling tetrahydrofuran for 3 h followed by evaporation and chromatography on silica gel with benzene as eluent yields a fraction from which orange 3 is readily crystallized since it is the least soluble component. However, preparative thin-layer chro-

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(4) By way of contrast it should be remembered that the reaction between meso-tetraphenylporphyrin (TPPH$_2$) and triruthenium dodecacarbonyl yields, after recrystallization from chloroform/ethanol, (TPP)Ru(CO)(C$_2$H$_5$OH): Cullen, D.; Meyer, E., Jr.; Srivastava, T. S.; Tsutsui, M. J. Chem. Soc., Chem. Commun. 1972, 584–585. Bonnett, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. J. Am. Chem. Soc. 1973, 95, 2141–2149.

Figure 1. Perspective drawing of **5**. Some selected bond distances: Ru–C(1), 1.878 (7) Å; Ru–C(2), 1.864 (6) Å; Ru–C(3), 2.086 (6) Å; Ru–N(1), 2.206 (5) Å; Ru–N(3), 2.257 (6) Å; Ru–N(4), 2.068 (5) Å.

Figure 2. Drawing which shows how the damaged porphyrin is wrapped about the ruthenium atom. Four phenyl groups are omitted in this drawing.

Scheme I

4   1   2, M = Fe
                                          3, M = Ru

matography of this fraction on silica gel with a 4:1 hexane/benzene eluent produces three bands, a rapidly eluting purple band followed by a red purple band and finally an orange band which contains 3. The relative amounts of material in these three fractions vary from preparation to preparation. Orange 3 is the predominant product and has been obtained in yields up to ca. 50%. It has been possible to obtain up to a 30% yield of crystals of the new compound 5[5] from the first band.

5

The composition and structure of **5** have been elucidated from an X-ray diffraction study.[6] Figure 1 presents a perspective view of the entire molecule while Figure 2 shows a different view which emphasizes the coordination environment about the ruthenium atom. These drawings show that the ruthenium atom has inserted itself into one of the pyrrole C–N bonds. The nonbonded C-(3)–N(1) separation is 2.741 (7) Å while the average bonded C–N distance in the unaltered pyrrole rings is 1.375 Å. On the other hand, the C(3)–Ru and N(1)–Ru distances of 2.086 (6) and 2.206 (5) Å, respectively, are consistent with the presence of C–Ru and N–Ru single bonds. The coordination sphere of the ruthenium atom consists of two pyrrole nitrogen atoms and two mutually cis carbonyl ligands in addition to the C and N atoms of the ruptured pyrrole ring. One pyrrole nitrogen atom, N(2), is not bound to ruthenium. As Figure 2 shows, the disrupted porphyrin is no longer planar.

Compound **5** is best formulated as a complex of Ru(II) with the macrocyclic ligand present as a dianion with carbanionic and amide characteristics at C(3) and N(1). As is usual for Ru(II), the ligands are arranged into approximately octahedral geometry with the three trans angles in the range 158.8–173.6° and the 12 cis angles falling in the range 76.0–102.8°.

The oxidative addition of C–N bonds to metal centers, which is seen in the formation of **2–5**, is a little studied and infrequently observed reaction. In contrast there are a number of examples in which low-valent metals are responsible for breaking C–P bonds.[7] Since C–N bond strengths are only about 10% greater than C–P bond strengths,[8] more examples of C–N bond fragmentation are likely to be discovered. The relatively rare observation of this reaction as contrasted to P–C bond disruption probably results from the fact that phosphines are widely studied as ligands with low-valent metals while amines are infrequently used as ligands for low-valent metals. The insertion of metals into C–N bonds, however, may be a significant part of the catalytic cycle where triruthenium dodecacarbonyl catalyzes the scrambling alkyl groups between two differently substituted tertiary amines.[9]

The biochemical significance of N-substituted and N,N′-bridged porphyrins has only recently begun to be recognized.[10] It remains to be seen whether insertion of metals into these substances under other conditions can produce carbon–nitrogen bond rupture. However, it should be noted that the major metabolic pathway for heme destruction involves an oxidative process in which the porphyrin periphery is attacked while the pyrrole rings remain intact.[11]

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Reaction of Nucleophiles with the Iron–Arene Complexes $(\eta^6\text{-}C_6R_6)_2Fe^{2+}$ and $(\eta^5\text{-}C_6R_6H)(\eta^6\text{-}C_6R_6)Fe^+$ (R = H, Me) and Functionalization of a Single Arene Ligand Using Hydride as a Protecting Group

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Nucleophilic addition of carbanions to coordinated arenes has been used successfully by Semmelhack as a means of functionalization in $(\eta^6\text{-arene})Cr(CO)_3$ complexes.[1] However, useful applications with other transition-metal activating groups are not known, although this area is promising as indicated by recent interesting reports with Mn[2] and Co[3] complexes. Dicationic arene complexes are of special interest because, in principle, they can react successively with two distinct nucleophiles to give functional cyclohexadiene complexes from which the ligands could be liberated by oxidation. However, the addition of carbon-centered nucleophiles apparently poses difficulties, as most previous reports concern the addition of hydride, phosphines, or phosphites.[4] Although addition of alkyl carbanions occasionally succeeds,[2,3] Vollhardt[3] showed that extension to functional carbanions is not possible with $Cp(\eta^6\text{-}C_6H_6)Co^{2+}$.

Our attention has focused on the easily available complexes $(arene)_2Fe^{2+}$.[5] In the case of $(1,3,5\text{-}Me_3C_6H_3)_2Fe^{2+}$, Helling showed that one nonfunctional carbanion can be added to each ring (with functional carbanions, the second addition does not occur[6b]):

$$\{(\eta^6\text{-}C_6H_3Me_3)Fe^{II}\}^{2+} \xrightarrow{2R^-} (\eta^5\text{-}C_6H_3Me_3R)Fe^{II}$$
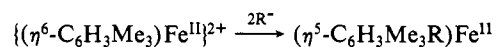
This regioselectivity (addition of the second carbanion to the even rather than to the odd ligand) was rationalized by Davies et al. in terms of charge control.[7] We suspected that this regioselectivity was in fact due to the peculiar 1, 3, 5 disposition

(5) Spectroscopic data: infrared, ν(CO), 2026, 1945 cm^{-1}; UV/vis, 384 nm (2.58 × 10^4 μ^{-1} cm^{-1}), 564 (1.35 × 10^4); ^{1}H NMR (CDCl$_3$), pyrrole, 9.41 (1 H, 10.3 Hz) d, 8.14 (1 H, 10.3 Hz) d, 7.65–7.4 (4 H) m, 7.10 (1 H, 3.8 Hz) d, 6.88 (1 H, 5.7 Hz) d; meso-phenyl, 8.11 (1 H, 4.9 Hz) d, 7.85 (2 H, 7.0 Hz) d, 7.80 (2 H, 6.8 Hz), 7.65–7.4 (14 H) m, 6.70 (1 H, 7.21 Hz) d; p-chlorophenyl, 7.03 (2 H, 7.7 Hz) d, 6.02 (2 H, 8.1 Hz) d, 5.66 (2 H, 7.7 Hz) d, 4.88 (2 H, 8.1 Hz) d.

(6) Single crystals of **5**·2CH$_2$Cl$_2$ were grown by diffusion of methanol into a dichloromethane solution of the complex. They belong to the space group P$\bar{1}$ (no. 2) with a = 9.796 (3) Å, b = 12.944 (4) Å, c = 22.377 (5) Å, α = 80.14 (2)°, β = 89.41 (2)°, γ = 70.25 (2)°, Z = 2 at 140 K. Refinement yielded R = 7.5% for 7658 reflections with $F > 6\sigma(F)$ and 677 parameters.

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