Substituent Effects on Rates of 4-*tert*-Butylpyridine Exchange in Ruthenium Carbonyl Complexes of Para-Substituted Tetraphenylporphyrins

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The rates of 4-*tert*-butylpyridine exchange in a series of ruthenium carbonyl para-substituted tetraphenylporphyrin 4-*tert*-butylpyridinates have been studied by variable-temperature ^{1}H NMR of the *tert*-butyl resonances. Activation parameters obtained by total line shape analysis are in the ranges $\Delta G^{\ddagger}_{298} = 18.5$–$19.8$ kcal/mol, $\Delta H^{\ddagger} = 19.6$–$22.1$ kcal/mol, and $\Delta S^{\ddagger} = 5.0$–$10.0$ eu. A plot of log rate vs. Hammett $4\sigma_p$ for the para substituent on the tetraphenylporphyrin gave a linear correlation with $\rho = -0.17$ at 25 °C.

Recent papers have shown that phenyl ring substituents in tetraphenylporphyrins influence rates of copper ion incorporation,[1] equilibrium constants for piperidine binding to Ni^{2+}, (VO)$^{2+}$, and Co^{2+} porphyrins,[2,3] equilibrium constants for pyridine coordination to Zn^{2+} and Co^{2+} porphyrins,[3,4] basicity and electronic spectra of free porphyrins,[5] and redox potentials for free porphyrins and Ni^{2+} and Co^{2+} porphyrins.[3,6] However, no reports have appeared concerning the effect of phenyl ring substituents on the kinetics of ligand exchange. This study concerns the effect of para substituents on the rate of 4-*tert*-butylpyridine exchange in a series of ruthenium carbonyl para-substituted tetraphenylporphyrin 4-*tert*-butylpyridinates, Ru(CO)(*p*-R-TPP)(*t*-Bupy).[7]

Experimental Section

Physical Measurements. Infrared spectra were recorded as Nujol or Halocarbon mulls on a Digilab IRS-10 Fourier transform IR spectrometer or Perkin-Elmer 710 or 337 grating spectrometers. Visible spectra were obtained in chloroform solutions, unless otherwise noted, on a Beckman Acta V spectrometer. Data are given below with wavelengths in nanometers and log ε in parentheses. ^{1}H NMR spectra were run at power levels well below saturation on a Varian HA-100 spectrometer equipped with a variable-temperature probe. Spectra were obtained with the spectrometer locked on the solvent resonance (1,1,2,2-tetrachloroethane). ^{1}H NMR chemical shifts were measured with respect to 1,1,2,2-tetrachloroethane and are reported below in ppm downfield of TMS using a correction of 5.96 ppm for the chemical shift of 1,1,2,2-tetrachloroethane at ca. 32 °C.

Preparation of Compounds. Porphyrins were prepared and characterized by literature methods: H$_2$(*p*-CF$_3$-TPP),[8] H$_2$(*p*-Cl-TPP),[9,10] H$_2$(*p*-Me-TPP),[9,10] H$_2$(*p*-*i*-Pr-TPP),[11] H$_2$(*p*-OMe-TPP),[9,10] and H$_2$(*p*-Et$_2$N-TPP).[12] Ru(CO)(OEP)(THF),[13] Ru(CO)(*p*-CF$_3$-TPP)(THF),[8] Ru(CO)(*p*-*i*-Pr-TPP)(*t*-Bupy),[11] and Ru(CO)-(TPP)(*t*-Bupy)[11] were prepared as previously reported.

Ru(CO)(*p*-R-TPP)(L); L = THF, EtOH, or H$_2$O. These complexes were prepared by the method reported for Ru(CO)(*p*-*i*-Pr-TPP)-(EtOH)[11] and purified by chromatography on Baker 0537 alumina. Details of reaction time, chromatography conditions, yield, and characterization data are given below for individual complexes.

Ru(CO)(*p*-Cl-TPP)(THF). Reaction time was 48 h. Chromatography: The crude complex was put on a column in CH$_2$Cl$_2$. Free porphyrin was eluted with CH$_2$Cl$_2$ and the complex eluted with 1:10 THF–CH$_2$Cl$_2$; yield 50%. IR: ν_{CO} 1950 cm^{-1}. Visible spectrum: 412 (5.48), 530 (4.41), 563 (3.55). ^{1}H NMR: pyrrole H, 8.66, singlet; *o*-H, 8.18, 8.03, doublets ($J \approx 8$ Hz); *m*-H, 7.72, 7.68, doublets ($J \approx 8$ Hz); THF, −0.50, −1.60, broad. Anal. Calcd for C$_{49}$H$_{32}$N$_4$O$_2$Cl$_4$Ru: C, 61.84; H, 3.39; N, 5.89; Cl, 14.90. Found: C, 61.86; H, 3.40; N, 6.08; Cl, 15.32. Although the Cl analysis was high for the THF adduct, a satisfactory Cl analysis was obtained for the *t*-Bupy adduct obtained from it.

Ru(CO)(*p*-Me-TPP)(EtOH). Reaction time was 36 h. Chromatography: The crude complex was put on a column in CH$_2$Cl$_2$. Free porphyrin was eluted with CH$_2$Cl$_2$ and the complex eluted with 1:10 EtOH–CH$_2$Cl$_2$; yield 72%. IR: ν_{CO} 1955 cm^{-1}. Visible spectrum: 413 (5.41), 531 (4.36), 564 (3.65). ^{1}H NMR: pyrrole H, 8.73, singlet; *o*-H, 8.12, 7.98, doublets ($J \approx 8$ Hz); *m*-H, 7.53, 7.50, doublets ($J \approx 8$ Hz); CH$_3$, 2.66, singlet; EtOH, −0.62, −1.73,

broad. Anal. Calcd for C$_{51}$H$_{42}$N$_4$O$_2$Ru: C, 72.58; H, 5.02; N, 6.64. Found: C, 72.77; H, 5.03; N, 6.71.

Ru(CO)(*p*-OMe-TPP)(THF). Reaction time was 37 h. Chromatography: The crude complex was put on a column in CH$_2$Cl$_2$. Free porphyrin was eluted with CH$_2$Cl$_2$ and the complex was eluted with 1:10 THF–CH$_2$Cl$_2$; yield 75%. IR: ν_{CO} 1935 cm^{-1}. Visible spectrum: 415 (5.41), 532 (4.37), 568 (3.70). ^{1}H NMR: pyrrole H, 8.69, singlet; *o*-H, 8.15, 8.06, doublets ($J \approx 8$ Hz); *m*-H, 7.20, 7.14, doublets ($J \approx 8$ Hz); CH$_3$, 3.97, singlet; THF, −0.34, −1.15, broad. Anal. Calcd for C$_{53}$H$_{44}$N$_4$O$_6$Ru: C, 68.15; H, 4.75; N, 6.00. Found: C, 68.29; H, 4.84; N, 6.20.

Ru(CO)(*p*-Et$_2$N-TPP)(H$_2$O). Reaction time was 17 h. Chromatography: The crude complex was put on a column in CHCl$_3$. CHCl$_3$ eluted the free porphyrin followed by the complex; yield 75%. IR: ν_{CO} 1935 cm^{-1}. Visible spectrum: 435 (5.17), 539 (4.29), 580 (4.17). ^{1}H NMR: pyrrole H, 8.88, singlet; *o*-H, 8.05, 7.98, doublets ($J \approx 8$ Hz); *m*-H, 7.03, broad doublet ($J \approx 8$ Hz); CH$_2$, 3.57, quartet; CH$_3$, 1.36, triplet. The elemental analysis for the compound denoted by Ru(CO)(*p*-Et$_2$N-TPP)(H$_2$O) does not fit any stoichiometry considered so far. The results are as follows: (a) Calcd for 1 H$_2$O: C, 70.16; H, 6.37; N, 10.73. Calcd for 2 H$_2$O: C, 68.97; H, 6.45; N, 10.55. (b) Found for sample recrystallized from CHCl$_3$ (and therefore possibly containing some EtOH as well as H$_2$O) and hexane: C, 69.79; H, 6.39; N, 10.71. Found for sample recrystallized from C$_2$HCl$_3$–hexane with H$_2$O present: C, 69.32; H, 6.29; N, 10.63. Found for new preparation of the complex recrystallized from CH$_2$Cl$_2$–hexane: C, 69.24; H, 6.36; N, 10.43. No EtOH, CHCl$_3$, or hexane was observable in the ^{1}H NMR spectra of these samples. Signals from CH$_2$Cl$_2$ and C$_2$HCl$_3$ would have been obscured by the large C$_2$H$_2$Cl$_4$ peak in these spectra. A search for OH bands in the IR spectrum did not yield any band assignable to H$_2$O. Previous examples also exist in which IR provided no evidence for the presence of H$_2$O when there was independent evidence for H$_2$O in the sample.[8,19,20] Until this surprising result can be explained, the exact constitution of many metalloporphyrin complexes must be considered uncertain as to the amount of H$_2$O present.

Adducts with 4-*tert*-butylpyridine were prepared by the method reported for Ru(CO)(*p*-*i*-Pr-TPP)(*t*-Bupy).[11] Characterization data for individual complexes are given below.

Ru(CO)(*p*-CF$_3$-TPP)(*t*-Bupy). IR: ν_{CO} 1955 cm^{-1}. Visible spectrum: 412 (5.49), 532 (4.29), 567 (3.56), 604 (3.21). ^{1}H NMR: pyrrole H, 8.57, singlet; *o*-H, 8.38, 8.17, doublets ($J \approx 8$ Hz); *m*-H, 8.00, 7.94, doublets ($J \approx 8$ Hz); *t*-Bupy, α-H, 1.40, doublet; β-H, 5.18, doublet; *t*-Bu, 0.36, singlet. Anal. Calcd for C$_{58}$H$_{37}$N$_5$F$_{12}$ORu: C, 60.63; H, 3.25; N, 6.09. Found: C, 60.56; H, 3.17; N, 6.11.

Ru(CO)(*p*-Cl-TPP)(*t*-Bupy). IR: ν_{CO} 1965 cm^{-1}. Visible spectrum: 414 (5.48), 533 (4.32), 566 (3.62). ^{1}H NMR: pyrrole H, 8.59, singlet; *o*-H, 8.16, 7.97, doublets ($J \approx 8$ Hz); *m*-H, 7.70, 7.65, doublets ($J \approx 8$ Hz); *t*-Bupy, α-H, 1.37, doublet; β-H, 5.14, doublet; *t*-Bu, 0.35, singlet. Anal. Calcd for C$_{54}$H$_{37}$N$_5$Cl$_4$ORu: C, 63.91; H, 3.68; N, 6.90; Cl, 13.97. Found: C, 64.04; H, 4.13; N, 6.80; Cl, 13.75. The slightly high H analysis is attributed to a small amount of heptane, remaining from C$_2$HCl$_3$–heptane recrystallization, which was observed in the NMR spectra despite prolonged drying in vacuo at ethanol reflux temperature.

Ru(CO)(*p*-Me-TPP)(*t*-Bupy). IR: ν_{CO} 1960 cm^{-1}. Visible spectrum: 414 (5.41); 534 (4.28); 570 (3.70). ^{1}H NMR: pyrrole H, 8.63, singlet; *o*-H, 8.12, 7.91, doublets ($J \approx 8$ Hz); *m*-H, 7.51,

7.45, doublets ($J \approx 8$ Hz); CH$_3$, 2.65, singlet; *t*-Bupy, α-H, 1.41; β-H, 5.10; *t*-Bu, 0.34. Anal. Calcd for C$_{58}$H$_{49}$N$_5$ORu: C, 74.65; H, 5.29; N, 7.51. Found: C, 74.63; H, 5.13; N, 7.47.

Ru(CO)(*p*-OMe-TPP)(*t*-Bupy). IR: ν_{CO} 1965 cm^{-1}. Visible spectrum: 417 (5.42), 535 (4.30), 572 (3.79). ^{1}H NMR: pyrrole H, 8.64, singlet; *o*-H, 8.15, 7.95, doublets ($J \approx 8$ Hz); *m*-H, 7.25, 7.19, doublets ($J \approx 8$ Hz); OCH$_3$, 4.06, singlet; *t*-Bupy, α-H, 1.42, doublet; β-H, 5.09, doublet; *t*-Bu, 0.33, singlet. Anal. Calcd for C$_{58}$H$_{49}$N$_5$O$_5$Ru: C, 69.86; H, 4.95; N, 7.02. Found: C, 69.87; H, 5.05; N, 7.11.

Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy). IR: ν_{CO} 1935 cm^{-1}. Visible spectrum: 435 (5.29), 542 (4.27), 585 (4.28). ^{1}H NMR: pyrrole H, 8.76, singlet; *o*-H, 8.08, 7.86, doublets ($J \approx 8$ Hz); *m*-H, 7.04, 6.98, doublets ($J \approx 8$ Hz); CH$_2$, 3.59, quartet; CH$_3$, 1.36, triplet; *t*-Bu, 0.33, singlet. Anal. Calcd for C$_{70}$H$_{77}$N$_9$ORu: C, 72.38; H, 6.68; N, 10.85. Found: C, 72.39; H, 6.76; N, 11.06.

Ru(CO)(OEP)(*t*-Bupy). IR: ν_{CO} 1935 cm^{-1}. Visible spectrum (benzene solution): 377 sh (4.65), 398 (5.48), 519 (4.22), 550 (4.41). ^{1}H NMR: *ms*-H, 9.85, singlet; CH$_2$, 4.04, quartet; CH$_3$, 1.88, triplet; *t*-Bupy, α-H, 0.82, doublet; β-H, 4.88, doublet; *t*-Bu, 0.24, singlet. Anal. Calcd for C$_{46}$H$_{57}$N$_5$ORu: C, 69.32; H, 7.21; N, 8.79. Found: C, 69.27; H, 7.01; N, 8.93.

Kinetic Analysis. ^{1}H NMR spectra were run on samples freshly prepared in an N$_2$ atmosphere using Ru(CO)(*p*-R-TPP)(*t*-Bupy) plus ca. 1 equiv of *t*-Bupy. Temperatures were calibrated after each set of data using methanol and ethylene glycol standards and the temperature-dependent shifts of Van Geet.[14] Temperature calibrations were reproducible to ± 0.5 °C. Temperatures are considered accurate to ± 1.5 °C. NMR spectra were recorded in the slow-exchange limit to determine the temperature dependence of nonexchanging chemical shift differences and line widths. Slow-exchange values were extrapolated through the exchange region. Plots of observed and extrapolated chemical shifts and line widths for the *tert*-butyl resonances in a mixture of *t*-Bupy and Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy) as a function of temperature are included as supplementary material. Line widths and chemical shifts for all the porphyrins studied were very similar. Simulated spectra were calculated by total line shape analysis using the Krieger–Lisle–Whitesides program EXCNMR.[15] τ(s) is defined as the mean preexchange lifetime of a *tert*-butyl group in a chemical shift environment. Thus $k = 1/\tau$ is the exchange rate in s^{-1} for exchange between coordinated and free *t*-Bupy. Calculated and observed spectra were visually compared and τ values are accurate to 5–10% except near the slow- and fast-exchange limits where uncertainties are ca. 20%. Activation parameters were determined from weighted least-squares fits to Arrhenius (ln ($1/\tau$) vs. $1/T$) and Eyring (ln ($h/kT\tau$) vs. $1/T$) equations.

Results and Discussion

^{1}H NMR spectra. The large diamagnetic anisotropy of the porphyrin ring causes substantial upfield shifts for protons above the plane of the ring. As a result, the chemical shift difference between the *tert*-butyl group of *t*-Bupy in Ru(CO)(*p*-R-TPP)(*t*-Bupy) and free *t*-Bupy is ca. 1 ppm. This large chemical shift difference allows rates of exchange between free and coordinated *t*-Bupy (reaction 1) to be monitored

Ru(CO)(*p*-R-TPP)(*t*-Bupy) + *t*-Bupy*
$$\rightleftharpoons \text{Ru(CO)(}p\text{-R-TPP)(}t\text{-Bupy*}) + t\text{-Bupy} \qquad (1)$$
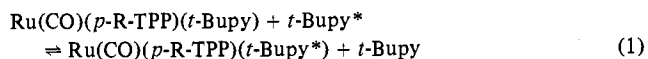
by variable-temperature ^{1}H NMR over a 80–100 °C temperature range. The large temperature interval permits more accurate evaluation of activation parameters than would be possible for exchange averaging of a small chemical shift difference.

Variable-temperature ^{1}H NMR spectra of the *t*-butyl resonances for Ru(CO)(*p*-R-TPP)(*t*-Bupy) in the presence of free *t*-Bupy in 1,1,2,2-tetrachloroethane solution were studied for R = CF$_3$, Cl, H, Me, *i*-Pr, OMe, and Et$_2$N. Prior work had shown that the rate of exchange of coordinated *t*-Bupy was independent of the overall concentration of the solution and independent of the ratio of free *t*-Bupy to coordinated *t*-Bupy.[11] In these studies concentrations of Ru(CO)(*p*-R-TPP)(*t*-Bupy) from 1.0 × 10^{-2} to 4.5 × 10^{-2} M were used (limited by solubilities and signal to noise ratio). Ratios of
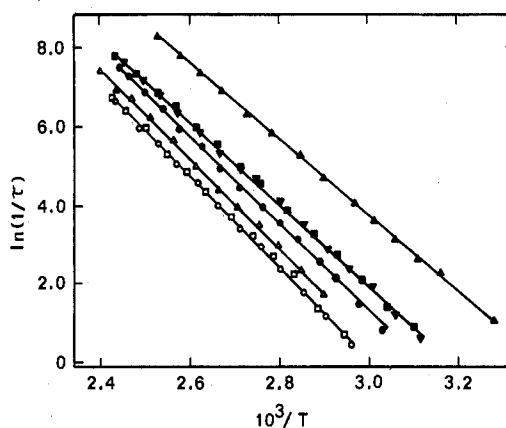

Figure 1. Arrhenius plots for pyridine exchange in Ru(CO)(*p*-R-TPP)(*t*-Bupy) and Ru(CO)(OEP)(*t*-Bupy): □, ○, two independent sets of data for R = CF$_3$; △, R = Cl; ●, R = OMe; ■, ▼, two independent sets of data for R = Et$_2$N; ▲, Ru(CO)(OEP)(*t*-Bupy).

Table I. Thermodynamic Parameters for Pyridine Exchange[a]

Porphyrin	$\Delta G^{\ddagger}_{298}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a kcal/mol
Ru(CO)(*p*-CF$_3$-TPP)(*t*-Bupy)[b]	19.8 ± 1.2[c]	22.1 ± 1.0	7.7 ± 2.5	22.8 ± 1.0
Ru(CO)(*p*-Cl-TPP)(*t*-Bupy)	19.4 ± 1.3	21.3 ± 1.0	6.5 ± 2.6	22.1 ± 1.0
Ru(CO)(TPP)-(*t*-Bupy)	19.1 ± 1.3	21.2 ± 1.0	7.0 ± 2.4	21.9 ± 1.0
Ru(CO)(*p*-Me-TPP)(*t*-Bupy)	19.0 ± 1.6	21.6 ± 0.9	8.7 ± 2.4	22.3 ± 1.0
Ru(CO)(*p*-*i*-Pr-TPP)(*t*-Bupy)	19.1 ± 1.3	21.9 ± 1.0	9.4 ± 2.7	22.7 ± 1.0
Ru(CO)(*p*-OMe-TPP)(*t*-Bupy)	19.0 ± 1.2	21.3 ± 0.7	7.7 ± 2.6	22.0 ± 0.7
Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy)[b]	18.5 ± 0.7	19.6 ± 0.6	4.9 ± 1.5	20.6 ± 0.6
Ru(CO)(OEP)-(*t*-Bupy)	17.3 ± 0.8	18.7 ± 0.6	4.8 ± 1.8	19.5 ± 0.6

[a] In 1,1,2,2-tetrachloroethane solutions. [b] Least-squares fit for two independent sets of data combined. [c] Uncertainties are given as ±3 standard deviations from the least-squares line.

free to coordinated *t*-Bupy were determined by simulation of the slow-exchange spectra and were 0.7–1.3 for the samples studied.

Line shape changes as a function of temperature were similar to those published previously for Ru(CO)(*p*-*i*-Pr-TPP)(*t*-Bupy) (Figure 1 of ref 11a). Electron-donating groups on the phenyl rings caused *t*-Bupy line shape changes to occur at lower temperatures and electron-withdrawing groups caused line shape changes to occur at higher temperatures. Rates as a function of temperature were determined by line shape analysis at 10–14 temperatures for each compound. To determine the reproducibility of the rate constants, variable-temperature spectra for Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy) and Ru(CO)(*p*-CF$_3$-TPP)(*t*-Bupy) were each obtained twice, on different preparations of the complex and on different days, and analyzed independently. In each case the two sets of data agreed very closely (see discussion of activation parameters.) Rates of *t*-Bupy exchange for Ru(CO)(OEP)(*t*-Bupy) were also obtained for comparison with the phenyl-substituted complexes.

Activation Parameters. Activation parameters were obtained by weighted least-squares fits of the experimental rate constants to the Arrhenius and Eyring equations. Arrhenius plots for several of the complexes are shown in Figure 1. In all cases there was no evidence of deviation from linearity, and correlation coefficients of 0.995 or better were obtained. Values of the activation parameters are given in Table I.
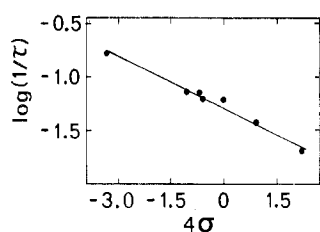
Figure 2. Plot of log (rate) vs. Hammett σ for *t*-Bupy exchange in Ru(CO)(*p*-R-TPP)(*t*-Bupy), reaction 1, at 25 °C.

Uncertainties are given as ±3 standard deviations from the weighted least-squares lines. Reproducibility, however, was considerably better than the stated uncertainties. Analysis of two independent sets of data for Ru(CO)(*p*-CF$_3$-TPP)(*t*-Bupy) gave $\Delta G^{\ddagger}_{298}$ = 19.8, 19.7, $\Delta H^{\ddagger}$ = 22.0, 22.1, $\Delta S^{\ddagger}$ = 7.6, 7.9, and E_a = 22.8, 22.8 and for Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy) gave $\Delta G^{\ddagger}_{298}$ = 18.4, 18.5, $\Delta H^{\ddagger}$ = 20.0, 19.9, $\Delta S^{\ddagger}$ = 5.1, 4.9, and E_a = 20.6, 20.7, with units as in Table I. The two sets of data in each case are shown in Figure 1. Values in Table I for these compounds were obtained for the two sets of data combined. Considering the excellent reproducibility of the parameters, it is felt that the small differences between the complexes are real and that comparisons are justified. It should also be noted that the uncertainty in $\Delta G^{\ddagger}_{298}$ is based on the uncertainty in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ since the kinetic data were extrapolated to 298 °C for tabulation whereas the coalescence temperatures were generally in the range 363–383 °C. Rates at individual points in the exchange region are known to considerably greater accuracy than might be indicated by the uncertainty in $\Delta G^{\ddagger}_{298}$.

Effect of Para Substituent. As seen from the plots in Figure 1, the changes in para substituent on the phenyl rings have considerable effect on the rate of *t*-Bupy exchange. At 70 °C the rate of exchange of *t*-Bupy in Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy) is about 5 times as fast as exchange in Ru(CO)(*p*-CF$_3$-TPP)(*t*-Bupy). However, the rate of exchange in Ru-(CO)(OEP)(*t*-Bupy) is considerably faster than for any of the substituted tetraphenylporphyrins and is about 5 times as fast as for Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy). The changes can also be seen in the values of $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$. Variations in $\Delta S^{\ddagger}$ are not systematic but are all in the range of 5–10 eu which is reasonable for a dissociative process which involves no separation of charges.

Studies of piperidine and pyridine binding to metal complexes of tetraarylporphyrins have found that the effects of para substituents correlate well with Hammett σ constants for the ring substituents.[2-4] We find that the rates of *t*-Bupy exchange in Ru(CO)(*p*-R-TPP)(*t*-Bupy) also correlate with Hammett σ_p values[16] for the R group as shown in Figure 2. A linear least-squares fit of log $(1/\tau)$ vs. 4σ gives ρ = –0.17 at 25 °C. Since data had to be extrapolated to obtain rates at 25 °C, a Hammett correlation was also done at 70 °C which is in the exchange-broadened region for all of the complexes. At 70 °C ρ = –0.13 and the Hammett plot is very similar to the one in Figure 2.

Electron-donating groups increase the rate of *t*-Bupy exchange. This result is consistent with the observation that electron-donating substituents on the phenyl rings cause free porphyrins to be more basic.[1] Since *t*-Bupy exchange has been shown to proceed by a dissociative pathway,[11] increased basicity of the porphyrin nitrogens and resultant weakening of the Ru–py interaction could lead to increased rates of exchange. Rates of *t*-Bupy exchange in Ru(CO)(OEP)(*t*-Bupy) are substantially faster than for any of the para-substituted tetraphenylporphyrin complexes. Thus, even with strongly electron-donating substituents on the phenyl rings, the tetraphenylporphyrins are considerably less basic than octaethylporphyrin. The greater basicity of OEP than of TPP has been noted previously.[17]

Para substitution in this series of complexes also has significant effect on the rate of rotation of the phenyl rings and on the electronic spectra. These effects are discussed elsewhere in conjunction with results for the titanyl analogues of the complexes reported here.[18]

Comparison with Equilibrium Constant Data. Recent papers have reported ρ values for the effect of para substituents on pyridine and piperidine binding to metal complexes of para-substituted tetraphenylporphyrins. Values of ρ for binding one axial ligand to Zn^{2+}, Ni^{2+}, Co^{2+}, and (VO)$^{2+}$ are 0.188,[4] 0.166,[2,3] 0.145,[3] and 0.112,[2] respectively. We find ρ = –0.17 for the rate of *t*-Bupy exchange in Ru(CO)(*p*-R-TPP)(*t*-Bupy). The similar magnitude but difference in sign between ρ values for equilibrium constants and for exchange rates is consistent with the dissociative nature of the exchange process, provided that the predominant effect of the substituent is on enthalpy rather than entropy. Larger values of K_{eq} reflect stronger binding of the ligand to the metalloporphyrin which would presumably result in slower exchange of the axial ligand.

Registry No. Ru(CO)(*p*-CF$_3$-TPP)(*t*-Bupy), 60840-41-7; Ru-(CO)(*p*-Cl-TPP)(*t*-Bupy), 60840-42-8; Ru(CO)(TPP)(*t*-Bupy), 39010-94-1; Ru(CO)(*p*-Me-TPP)(*t*-Bupy), 60909-08-2; Ru(CO)-(*p*-i-Pr-TPP)(*t*-Bupy), 34714-21-1; Ru(CO)(*p*-OMe-TPP)(*t*-Bupy), 60882-60-2; Ru(CO)(*p*-Et$_2$N-TPP)(*t*-Bupy), 60860-92-6; Ru-(CO)(OEP)(*t*-Bupy), 55059-72-8; Ru(CO)(*p*-Cl-TPP)(THF), 60860-93-7; Ru(CO)(*p*-Me-TPP)(EtOH), 60860-94-8; Ru(CO)-(*p*-OMe-TPP)(THF), 60860-95-9; Ru(CO)(*p*-Et$_2$N-TPP)(H$_2$O), 60882-59-9.

Supplementary Material Available: Plots of the temperature dependence of chemical shifts and line widths (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. Moet-Ner and A. D. Adler, *J. Am. Chem. Soc.*, **94**, 4763 (1972).
(2) F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).
(3) F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3484 (1976).
(4) G. C. Vogel and B. A. Beckman, *Inorg. Chem.*, **15**, 483 (1976).
(5) M. Moet-Ner and A. D. Adler, *J. Am. Chem. Soc.*, **97**, 5107 (1975).
(6) K. M. Kadish and M. M. Morrison, *J. Am. Chem. Soc.*, **98**, 3326 (1976); *Inorg. Chem.*, **15**, 980 (1976).
(7) Abbreviations used throughout: *t*-Bupy, 4-*tert*-butylpyridine; Ru-(CO)(*p*-R-TPP), ruthenium carbonyl tetrakis(*p*-R-phenyl)porphyrin; *p*-CF$_3$-TPP, tetrakis(*p*-trifluoromethylphenyl)porphyrin dianion; *p*-Cl-TPP, tetrakis(*p*-chlorophenyl)porphyrin dianion; *p*-Me-TPP, tetrakis(*p*-methylphenyl)porphyrin dianion; *p*-i-Pr-TPP, tetrakis(*p*-isopropyl-phenyl)porphyrin dianion; *p*-OMe-TPP, tetrakis(*p*-methoxyphenyl)-porphyrin dianion; *p*-Et$_2$N-TPP, tetrakis(*p*-diethylaminophenyl)porphyrin dianion; OEP, octaethylporphyrin.
(8) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **97**, 3660 (1975).
(9) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).
(10) D. W. Thomas and A. E. Martell, *J. Am. Chem. Soc.*, **78**, 1338 (1956).
(11) (a) S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organomet. Chem.*, **32**, C52 (1971); (b) *ibid.*, **39**, 179 (1972).
(12) N. Datta-Gupta and T. J. Bardos, *J. Heterocycl. Chem.*, **3**, 495 (1966).
(13) G. R. Eaton and S. S. Eaton, *J. Am. Chem. Soc.*, **97**, 235 (1975).
(14) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).
(15) J. Krieger, Ph.D. Thesis, Massachusetts Institute of Technology, 1971; J. S. Lisle, S.B. Thesis, Massachusetts Institute of Technology, 1968; G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **89**, 2855 (1967).
(16) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963, p 204.
(17) G. N. La Mar, *J. Am. Chem. Soc.*, **95**, 1662 (1973).

(18) S. S. Eaton and G. R. Eaton, to be submitted for publication.
(19) J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage, and D. Weck, *Justus Liebigs Ann. Chem.*, **745**, 135 (1971); J. W. Buchler,

L. Puppe, and H. H. Schneehage, *ibid.*, **749**, 134 (1971).
(20) R. J. Abraham, G. H. Bennett, and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, 2142 (1973).

Preparation and Characterization of Members of a Homologous Series of Dihydridocarbonyl Compounds of Osmium

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The carbonyl hydrides $H_2[Os(CO)_4]_n$ ($n = 1$, 2, or 3) have been prepared by the high-pressure carbonylation of osmium tetroxide in the presence of hydrogen. We also present evidence for the formation of $H_2Os_4(CO)_{16}$ in this reaction. The dihydrides $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$ have also been obtained by the reduction of the dihalides $Os_2X_2(CO)_8$ and $Os_3X_2(CO)_{12}$ (X = Cl or Br). Ir, NMR, and mass spectra are reported and discussed for the compounds, with particular reference to the structures of these hydrides.

Introduction

The preparation of osmium carbonyls by carbonylation of osmium tetroxide was first reported by Hieber and Stallman in 1943.[2] In the preparation of osmium pentacarbonyl, they observed a more volatile component which they assumed to be $H_2Os(CO)_4$, although it was not fully characterized at the time. These reactions were reinvestigated by L'Eplattenier and Calderazzo, who prepared and characterized the pentacarbonyl[3] and later the dihydride, $H_2Os(CO)_4$.[4] More recently, trinuclear $H_2Os_3(CO)_{10}$,[5,6] $H_2Os_3(CO)_{11}$,[7,8] and $HOs_3(CO)_{12}^+$,[9,10] tetranuclear $H_4Os_4(CO)_{12}$[5,6] and $H_2Os_4(CO)_{13}$,[5] pentanuclear $H_2Os_5(CO)_{16}$[11] and $H_2Os_5(CO)_{15}$,[11] and hexanuclear $H_2Os_6(CO)_{18}$[11] have been prepared by a variety of synthetic routes, thus demonstrating the rich carbonyl–hydride chemistry of osmium.

We now report in detail on the preparation and characterization of the new dihydrides $H_2Os_2(CO)_8$ and $H_2Os_3(CO)_{12}$ and present evidence for $H_2Os_4(CO)_{16}$. These hydrides are members of the homologous series $H_2[Os(CO)_4]_n$. We have already reported briefly on these compounds in preliminary communications.[12,13]
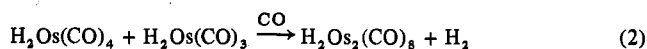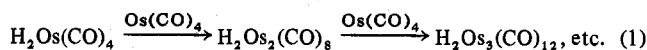
Results and Discussion

L'Eplattenier and Calderazzo reported that almost quantitative yields of $H_2Os(CO)_4$ were obtained by the high-pressure carbonylation of osmium tetroxide in the presence of hydrogen.[4] Operating under conditions slightly different from those reported previously[4] and using a longer reaction time, we find that although $H_2Os(CO)_4$ is the main product of this reaction, other products are also formed. Thus after completion of the carbonylation reaction of osmium tetroxide in the presence of hydrogen, the heptane solution of the volatile products was collected in a liquid nitrogen trap. An ir spectrum of this solution in the $\nu(CO)$ region showed it to be mainly $H_2Os(CO)_4$ with traces of $Os(CO)_5$, as had been found previously.[4] However, we find an oily solid residue remains in the autoclave, the ir spectrum of which shows many bands in the $\nu(CO)$ region. Separation of this mixture by fractional sublimation and recrystallization (see Experimental Section) give the compounds $H_2Os_2(CO)_8$, $H_2Os_3(CO)_{12}$, and $Os_3(CO)_{12}$ and traces of $H_2Os_4(CO)_{16}$.

We also find that the dihydrides $H_2[Os(CO)_4]_n$ ($n = 2$ or 3) can be prepared by the reduction of the corresponding dihalides $X_2[Os(CO)_4]_n$ (X = Cl or Br). Although this route is of little preparative use for $H_2Os_2(CO)_8$, since the dihalide

was itself prepared from the dihydride,[12] we find it to be a useful method for the preparation of the trinuclear hydride $H_2Os_3(CO)_{12}$, since the dihalides $Os_3X_2(CO)_{12}$ (X = Cl or Br) are readily available from the reactions of halogens with $Os_3(CO)_{12}$.[5] Using the reducing agent, sodium borohydride in methanol, only low yields of $H_2Os_3(CO)_{12}$ were obtained from $Os_3X_2(CO)_{12}$. This may be contrasted with the report of other workers who obtained low yields of $HOs_3Cl(CO)_{10}$ by the reduction of $Os_3Cl_2(CO)_{12}$ with sodium borohydride in tetrahydrofuran.[14] We find that use of the reducing system zinc dust/acetic acid/methanol results in good yields of the dihydrides. For example, reduction of $Os_3Br_2(CO)_{12}$ gives 90% yield of $H_2Os_3(CO)_{12}$. A modification of this reduction using acetic-d_4 acid and methanol-d was used to prepare the dideuterides $D_2[Os(CO)_4]_n$ ($n = 2$ or 3); in the case of $D_2Os_2(CO)_8$, a slightly impure product was obtained even after repeated distillations.

Several routes to the dihydrides $H_2[Os(CO)_4]_n$ ($n = 2$, 3, or 4) under the reaction conditions in the autoclave seem possible.

(1) Reaction of $H_2Os(CO)_4$ with the Coordinatively Unsaturated Intermediates $Os(CO)_4$ or $H_2Os(CO)_3$.

$$H_2Os(CO)_4 \xrightarrow{Os(CO)_4} H_2Os_2(CO)_8 \xrightarrow{Os(CO)_4} H_2Os_3(CO)_{12}, \text{etc.} \quad (1)$$

$$H_2Os(CO)_4 + H_2Os(CO)_3 \xrightarrow{CO} H_2Os_2(CO)_8 + H_2 \quad (2)$$

Equation 1 involves insertion of $Os(CO)_4$ into osmium–hydrogen bonds and represents the reverse of the reaction we suggested for the thermal decomposition of $H_2Os_3(CO)_{12}$.[13] Recently, it has been shown that the primary product of the thermal decomposition of $H_2Os(CO)_4$ is $H_2Os_2(CO)_8$, eq 2.[15] Under the conditions of the autoclave reaction, $H_2Os(CO)_3$ could be formed from the carbonylation of osmium tetroxide in the presence of hydrogen rather than dissociation of carbon monoxide from $H_2Os(CO)_4$, and $Os(CO)_4$ could be formed directly from the reaction of osmium tetroxide and carbon monoxide.

(2) Reaction of $Os_2(CO)_9$ with Hydrogen.

$$Os_2(CO)_9 + H_2 \rightarrow H_2Os_2(CO)_8 + CO \quad (3)$$
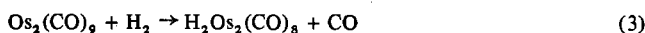
The dinuclear carbonyl $Os_2(CO)_9$ may have a fleeting existence in the autoclave reaction and is presumably an intermediate in the formation of $Os_3(CO)_{12}$ from $Os(CO)_5$. We have isolated $Os_2(CO)_9$[16] and shown that it reacts with hy-