Table III. Bond Lengths (Å) in the Coordination Group, Porphinato Skeleton, and Pyridine Ligands of $Cr(py)_2(TPP)$[a]

Cr_1-N_1	2.026 (8)	$C_{a5}-C_{m5}$	1.372 (12)
Cr_1-N_2	2.012 (8)	$C_{a6}-C_{b6}$	1.410 (12)
Cr_1-N_3	2.141 (8)	$C_{a6}-C_{m4}$	1.401 (12)
Cr_2-N_4	2.044 (8)	$C_{a7}-C_{b7}$	1.441 (13)
Cr_2-N_5	2.026 (8)	$C_{a7}-C_{m4}$	1.368 (12)
Cr_2-N_6	2.121 (8)	$C_{a8}-C_{b8}$	1.441 (13)
N_1-C_{a1}	1.408 (11)	$C_{a8}-C_{m5}$	1.402 (12)
N_1-C_{a2}	1.391 (12)	$C_{b1}-C_{b2}$	1.345 (13)
N_2-C_{a3}	1.367 (12)	$C_{b3}-C_{b4}$	1.336 (14)
N_2-C_{a4}	1.379 (11)	$C_{b5}-C_{b6}$	1.355 (13)
N_4-C_{a5}	1.399 (11)	$C_{b7}-C_{b8}$	1.347 (13)
N_4-C_{a6}	1.380 (11)	N_3-C_{15}	1.341 (12)
N_5-C_{a7}	1.378 (11)	N_3-C_{19}	1.349 (13)
N_5-C_{a8}	1.400 (11)	$C_{15}-C_{16}$	1.394 (15)
$C_{a1}-C_{b1}$	1.424 (13)	$C_{16}-C_{17}$	1.367 (17)
$C_{a1}-C_{m3}$	1.388 (11)	$C_{17}-C_{18}$	1.406 (17)
$C_{a2}-C_{b2}$	1.438 (13)	$C_{18}-C_{19}$	1.443 (15)
$C_{a2}-C_{m1}$	1.398 (13)	N_6-C_{32}	1.334 (12)
$C_{a3}-C_{b3}$	1.439 (14)	N_6-C_{36}	1.349 (11)
$C_{a3}-C_{m1}$	1.394 (13)	$C_{32}-C_{33}$	1.419 (14)
$C_{a4}-C_{b4}$	1.432 (14)	$C_{33}-C_{34}$	1.433 (15)
$C_{a4}-C_{m2}$	1.374 (11)	$C_{34}-C_{35}$	1.419 (15)
$C_{a5}-C_{b5}$	1.425 (12)	$C_{35}-C_{36}$	1.409 (14)

[a] The figures in parentheses are the estimated standard deviations in the least significant figure.

Table IV. Bond Angles (deg) in the Coordination Group and Porphinato Skeleton of $Cr(py)_2(TPP)$[a]

$N_1Cr_1N_2$	90.1 (3)	$N_4C_{a6}C_{m4}$	124.2 (10)
$N_1Cr_1N_1''$	89.4 (5)	$C_{m4}C_{a6}C_{b6}$	127.2 (10)
$N_2Cr_1N_2''$	90.5 (5)	$N_5C_{a7}C_{b7}$	109.2 (9)
$N_1Cr_1N_3$	88.0 (3)	$N_5C_{a7}C_{m4}$	126.7 (10)
$N_2Cr_1N_3$	91.0 (3)	$C_{m4}C_{a7}C_{b7}$	124.1 (10)
$N_4Cr_2N_5'$	90.4 (3)	$N_5C_{a8}C_{b8}$	108.6 (9)
$N_4Cr_2N_5$	89.6 (3)	$N_5C_{a8}C_{m5}$	124.7 (10)
$N_4Cr_2N_6$	91.0 (3)	$C_{m5}C_{a8}C_{b8}$	126.7 (10)
$N_5Cr_2N_6$	90.8 (3)	$C_{a1}C_{b1}C_{b2}$	108.4 (10)
$C_{a1}N_1C_{a2}$	106.5 (9)	$C_{a2}C_{b2}C_{b1}$	108.2 (10)
$C_{a3}N_2C_{a4}$	105.2 (9)	$C_{a3}C_{b3}C_{b4}$	105.0 (11)
$C_{a5}N_4C_{a6}$	107.2 (8)	$C_{a4}C_{b4}C_{b3}$	109.3 (10)
$C_{a7}N_5C_{a8}$	106.6 (8)	$C_{a5}C_{b5}C_{b6}$	107.6 (10)
$N_1C_{a1}C_{b1}$	108.5 (9)	$C_{a6}C_{b6}C_{b5}$	108.7 (10)
$N_1C_{a1}C_{m3}$	125.0 (1)	$C_{a7}C_{b7}C_{b8}$	107.8 (10)
$C_{m3}C_{a1}C_{b1}$	126.5 (10)	$C_{a8}C_{b8}C_{b7}$	107.7 (10)
$N_1C_{a2}C_{b2}$	108.5 (10)	$C_{a2}C_{m1}C_{a3}$	125.4 (10)
$N_1C_{a2}C_{m1}$	125.5 (10)	$C_{a4}C_{m2}C_{a4}''$	127.3 (14)
$C_{m1}C_{a2}C_{b2}$	125.0 (10)	$C_{a1}C_{m3}C_{a1}''$	125.5 (14)
$N_2C_{a3}C_{b3}$	111.6 (10)	$C_{a6}C_{m4}C_{a7}$	126.4 (10)
$N_2C_{a3}C_{m1}$	124.6 (11)	$C_{a5}'C_{m5}C_{a8}$	125.2 (10)
$C_{m1}C_{a3}C_{b3}$	123.7 (11)	$Cr_1N_1C_{a1}$	127.5 (7)
$N_2C_{a4}C_{b4}$	108.9 (10)	$Cr_1N_1C_{a2}$	126.0 (7)
$N_2C_{a4}C_{m2}$	124.5 (11)	$Cr_1N_2C_{a3}$	128.2 (8)
$C_{m2}C_{a4}C_{b4}$	125.6 (11)	$Cr_1N_2C_{a4}$	126.6 (8)
$N_4C_{a5}C_{b5}$	107.9 (9)	$Cr_2N_4C_{a5}$	126.0 (7)
$N_4C_{a5}C_{m5}'$	126.8 (10)	$Cr_2N_4C_{a6}$	126.4 (7)
$C_{m5}'C_{a5}C_{b5}$	125.3 (10)	$Cr_2N_5C_{a7}$	125.6 (7)
$N_4C_{a6}C_{b6}$	108.5 (9)	$Cr_2N_5C_{a8}$	127.7 (7)

[a] The numbers in parentheses are the estimated standard deviations in the least significant figure.

for further consideration. This axial distance is considerably shorter than that observed in the isoelectronic manganese(III) porphyrins. In Mn(Cl)(py)(TPP),[12] the Mn–N(py) bond distance is 2.444 (4) Å, and in $[Mn(1\text{-}MeIm)_2(TPP)]^+$,[13] the Mn–N(Im) bond distance is 2.308 (3) Å. This difference in the axial bond lengths is attributable[3] to the population of the $3d_{z^2}$ orbital in the high-spin Mn(III) derivatives and its depopulation in the low-spin Cr(II) complex.

The average chromium–porphinato nitrogen bond distance is 2.027 (13) Å, comparable to the 2.033 (1) Å Cr–N bond distance observed in four-coordinate Cr(TPP)·2(toluene).[4] Thus although the addition of two axial pyridine ligands to Cr(TPP) leads to a high-spin to low-spin conversion, there is little change in the equatorial coordination parameters, since both complexes contain an unoccupied $d_{x^2-y^2}$ orbital. A similar high to low spin conversion was observed by Tsutsui et al.,[14] who noted that chromium(II) mesoporphyrin IX dimethyl ester was high spin in solution and low spin in the solid state. Presumably, in the solid state intermolecular interactions lead to six-coordinate species. As noted previously,[4] the chromium–porphinato nitrogen bond distances in the chromium(II) porphyrins appear short compared to the one other known Cr(II) structure[15] and also to known Cr(III)–N bond distances.[16] This emphasizes, as in other porphinato derivatives, the strong complexing nature of the porphinato ligand.

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Supplementary Material Available: Table II, rigid-body parameter listings, Figures 3 and 4, formal diagrams of the porphyrin cores showing the displacement of each atom from the mean plane of the core, and listings of the observed and calculated structure factor amplitudes (×10) (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Notre Dame. (b) University of Southern California.

(2) Cheung, S. K.; Grimes, C. J.; Wong, J.; Reed, C. A. *J. Am. Chem. Soc.* **1976**, *98*, 5028–9.

(3) Scheidt, W. R. *Acc. Chem. Res.* **1977**, *10*, 339–45.

(4) Scheidt, W. R.; Reed, C. A. *Inorg. Chem.* **1978**, *17*, 710–4.

(5) Reed, C. A.; Kouba, J. K.; Grimes, C. J.; Cheung, S. K. *Inorg. Chem.* **1978**, *17*, 2666–70.

(6) Blessing, R.; Coppens, P.; Becker, P. *J. Appl. Crystallogr.* **1974**, 488–92.

(7) Scheidt, W. R. *J. Am. Chem. Soc.* **1974**, *96*, 84–9.

(8) Kirner, J. F.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977**, *99*, 1093–101.

(9) In addition to various local programs, modified versions of the following programs were employed: Busing and Levy's ORFLS least squares, Johnson's ORTEP2 thermal ellipsoid plotting program, Hubbard, Quicksall, and Jacobson's ALFF Fourier program, and Busing and Levy's ORFFE error function program.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–3. Scattering factors for hydrogen were taken from Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87. Real and imaginary corrections for anomalous dispersion in the form factor for chromium were from Cromer and Liberman: Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–8.

(11) Scheidt, W. R. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 10. Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975, Chapter 8.

(12) Kirner, J. F.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 2081–6.

(13) Steffen, W. L.; Chen, H. K.; Hoard, J. L.; Reed, C. A. "Abstracts of Papers", 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978; American Chemical Society: Washington, D.C., 1978; INOR 15.

(14) Tsutsui, M.; Velapoldi, R. A.; Suzuki, K.; Vohwinkel, F.; Iehikawa, M.; Koyano, T. *J. Am. Chem. Soc.* **1969**, *91*, 6262–6.

(15) Bradley, D. C.; Hursthouse, M. B.; Newing, C. W.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 567–8.

(16) See footnote 17 of ref 4.

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Kinetics of the Reaction between Bis(O-substituted xanthato)nickel(II) and 2,2′-Bipyridine in Benzene

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Grant and co-workers, in a series of related papers,[1] have studied the kinetics and the mechanism of the addition of bidentate bases to several nickel(II) complexes; in particular these authors have examined the effect of substituents at the

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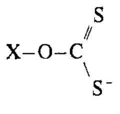
ligand in the plane upon the rate of addition of 1,10-phenanthroline to bis(thioacetylacetonato)nickel(II) and bis(O,O′-disubstituted phosphorodithioato-*S*,*S*′)nickel(II) complexes.

In order to investigate further such an effect and in continuing our previous kinetic studies on square-planar–octahedral interconversion of nickel(II) complexes,[2] we have undertaken a kinetic study of reaction 1 in benzene at 25 °C.

$$\mathrm{Ni(X\text{-}xanthate)_2 + bpy \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ni(X\text{-}xanthato)_2(bpy)} \tag{1}$$



$\mathrm{X{-}O{-}C({=}S){-}S^-}$

X = methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, benzyl, cyclohexyl, allyl, 2,6-dimethylphenyl, methoxyethyl

Bis(O-substituted xanthato)nickel(II) complexes yield octahedral adducts, presumably of cis configuration[3,4] on adding bipyridine.

This paper reports the forward, k_f, and reverse, k_r, rate constants for reaction 1 in benzene at 25 °C; activation parameters associated with the same reaction, when X is cyclohexyl, are also presented. Furthermore, the equilibrium constants at 25 °C for addition of two molecules of pyridine to complexes $\mathrm{Ni(Xxan)_2}$ (X = *n*-butyl, *sec*-butyl, allyl, methoxyethyl; xan = xanthate) are reported.

Experimental Section

Materials. Nickel xanthates were prepared according to the methods reported in the literature;[5,6] $\mathrm{Ni(allyl\ xanthate)_2}$ could not be crystallized, and the dark brown solid which precipitated on mixing aqueous solutions of potassium xanthate and nickel(II) nitrate was dried and used without further purification. Ni(*sec*-butyl xanthate)$_2$ was obtained as a dark oil which was extracted with benzene and then dried for 2 days over phosphorus pentoxide under vacuum. The resulting dark brown microcrystalline mass was used without further purification. All the other nickel xanthates were recrystallized twice from acetone.

Zinc xanthates were obtained by addition[5] of aqueous solutions of the appropriate xanthate to a solution of zinc chloride in water. The light yellow compounds were recrystallized when possible from acetone.

The purity of the compounds was checked by elemental analysis and IR spectra.[5,6] 2,2′-Bipyridine was of reagent grade. Benzene was dried over calcium hydride and then distilled.

Thermodynamics. The formation constants for the adducts $\mathrm{Ni(Xxan)_2(py)_2}$ in benzene were determined spectrophotometrically[7] by use of an Optica CF 4R recording spectrophotometer equipped with a thermostated cell holder. The details of the experimental procedure have been described elsewhere.[2]

Kinetics. The rates of reaction were followed spectrophotometrically by measuring the changes in optical density of the reaction mixtures in dependence on time. A Beckman DU spectrophotometer equipped with a Saitron 301 photometer and a Servogor 5 recording potentiometer was used to follow the slower reactions. The reactants were mixed in a thermostated quartz cell, and the rate of the reaction was monitored by the variation of the absorbance of the mixture (at a suitable wavelength in the visible region) as a function of time. The rate constants were calculated from the slope of the usual plot of log $(A_\infty - A_t)$ vs. time, where A_∞ represents the absorbance after 6–8 half-lives and A_t the absorbance at various times. Faster reactions were followed by means of a stopped-flow Durrum D-110 provided with a Kel-F flow system. The exponential traces were photographed, and the values of k_{obsd} were evaluated by matching the experimental traces with similar ones produced by an exponential generator[8] on the same oscilloscope. Each value of k_{obsd} is at least the average of three experiments. The kinetic experiments for the forward path of reaction 1 were performed under pseudo-first-order conditions with 2,2′-bipyridine in at least a 10-fold excess over the nickel complex concentration;[9] six or more kinetic runs, at different 2,2′-bipyridine concentration, were performed for each nickel complex. For kinetic measurements of the dissociation rate constants $\mathrm{Zn(xan)_2}$ was used to drive the reaction: the concentrations of $\mathrm{Ni(xan)_2}$ and 2,2′-bipyridine were kept constant at 5×10^{-5} M and the zinc xanthate concentrations varied in four steps from 5×10^{-4} to 3.0×10^{-3} M. All the kinetic values were reproducible to better than ±10%.

Table I. Values of Rate Constants k_f and k_r for Reaction 1 and Values of Equilibrium Constants K_{py} for Reaction 6 in Benzene at 25 °C

substituent, X	$\Sigma\sigma^*$ [a]	$10^{-4}k_f$, $\mathrm{M^{-1}\ s^{-1}}$	10^2k_r, $\mathrm{s^{-1}}$	log (k_f/k_r)	log [K_{py} ($\mathrm{M^{-2}}$)]
methyl	0	6.67 ± 0.26	1.00 ± 0.06	6.82	3.97[b]
ethyl	−0.2	3.35 ± 0.13	2.11 ± 0.06	6.20	3.44[b]
n-propyl	−0.23	3.23 ± 0.09	2.80 ± 0.04	6.06	1.87[b]
isopropyl	−0.38	1.73 ± 0.02	5.41 ± 0.08	5.51	2.69[b]
n-butyl	−0.26	2.87 ± 0.04	2.90 ± 0.04	6.00	3.24
sec-butyl	−0.38	1.57 ± 0.05	6.21 ± 0.32	5.40	2.58
benzyl	+0.54	6.29 ± 0.18	1.40 ± 0.12	6.65	3.86[b]
cyclohexyl	−0.30	1.73 ± 0.05	5.62 ± 0.24	5.49	2.66[b]
allyl	+1.12	5.55 ± 0.16	1.55 ± 0.09	6.55	3.72
methoxyethyl		6.16 ± 0.24	1.55 ± 0.04	6.60	3.74
2,6-dimethylphenyl		3.17 ± 0.09			

[a] Sum of the Taft σ^* values[11] relative to the substituents X in the complexes $\mathrm{Ni(Xxan)_2}$. [b] Values from ref 10.

Results

The values of the forward rate constants, k_f, were obtained by studying the dependence of the rate of reaction between $\mathrm{Ni(xan)_2}$ and 2,2′-bipyridine on the 2,2′-bipyridine concentration. Good straight lines with zero intercepts were obtained in each case by plotting the values of k_{obsd} against those of bpy concentration. The experimental results are therefore in agreement with the rate law

$$k_{\mathrm{obsd}} = k_f[\mathrm{bpy}] \tag{2}$$

The gradients of the plots k_{obsd} vs. [bpy], obtained by least-squares treatment, yielded the values of k_f. These values are reported in Table I. The values of rate constants, k_r, for the dissociation of the octahedral adducts were obtained by driving the reverse reaction with $\mathrm{Zn(xan)_2}$

$$\mathrm{Ni(Xxan)_2(bpy) \underset{k_f}{\overset{k_r}{\rightleftarrows}} Ni(Xxan)_2 + bpy} \tag{3}$$

$$\mathrm{Zn(Xxan)_2 + bpy \xrightarrow{k_1} Zn(Xxan)_2(bpy)} \tag{4}$$

The $\mathrm{Zn(Xxan)_2}$ concentration was in each case much larger than that of $\mathrm{Ni(Xxan)_2(bpy)}$; under these experimental conditions and owing to the fact that $k_1 > k_f$,[12] the values of k_{obsd} were independent of $\mathrm{Zn(Xxan)_2}$ concentration and were equal to those of k_r. In fact, it can be shown[13] that, when $k_1[\mathrm{Zn(Xxan)_2}] \gg k_f[\mathrm{Ni(Xxan)_2}]$, k_{obsd} equals k_r. The values of k_r, which are the average of four values obtained at different $\mathrm{Zn(Xxan)_2}$ concentrations, are reported in Table I.

Activation parameters for the reaction

$$\mathrm{Ni(cyclohexyl\ xanthate)_2 + bpy \underset{k_r}{\overset{k_f}{\rightleftarrows}} Ni(cyclohexyl\ xanthate)_2bpy} \tag{5}$$

have been determined by studying the temperature dependence of k_f and k_r. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for both the forward and reverse paths of the reaction have been obtained by least-squares analysis of the usual Arrhenius plots and are quoted in Table II.

The equilibrium constants, K_{py} ($\mathrm{M^{-2}}$), for the reaction

$$\mathrm{Ni(Xxan)_2 + 2py \rightleftarrows Ni(Xxan)_2(py)_2} \tag{6}$$

$$K_{py} = [\mathrm{Ni(Xxan)_2(py)_2}]/([\mathrm{Ni(Xxan)_2}][\mathrm{py}]^2) \tag{7}$$

(X = *n*-butyl, *sec*-butyl, allyl, methoxyethyl) in benzene at 25 °C, which were determined spectrophotometrically (see Experimental Section), are reported in Table I.

Table II. Values of Rate Constants and Activation Parameters for Reaction 5 in Benzene

T, °C	$10^{-4}k_f$, $M^{-1}\ s^{-1}$	10^2k_r, s^{-1}	T, °C	$10^{-4}k_f$, $M^{-1}\ s^{-1}$	10^2k_r, s^{-1}
15	1.17 ± 0.05	1.46 ± 0.07	30	1.97 ± 0.17	12.70 ± 1.08
20	1.39 ± 0.03	3.00 ± 0.13	35	2.30 ± 0.11	23.30 ± 0.84
25	1.73 ± 0.09	5.62 ± 0.24			

$\Delta H_f^{\ddagger} = 5.4 \pm 0.6$ kcal mol^{-1}
$\Delta H_r^{\ddagger} = 24 \pm 1$ kcal mol^{-1}
$\Delta S_f^{\ddagger} = -21 \pm 4$ cal K^{-1} mol^{-1}
$\Delta S_r^{\ddagger} = +26 \pm 3$ cal K^{-1} mol^{-1}

Discussion

The main feature emerging from inspection of Table I is that the rate constants for both the forward and reverse reactions are dependent on the nature of the substituent X at the ligand in the plane. In particular, one may note that, on increasing the σ-donor ability of the alkyl substituents, the values of the forward rate constant, k_f, decrease and those of the dissociation rate constant, k_r, increase; therefore, the electrophilicity of the nickel atom is directly related to the nature of the group X. This result, which is in line with previous findings on the solvent exchange on various octahedral nickel(II) complexes[14,15] and on the addition of 1,10-phenanthroline to bis(thioacetylacetonato)nickel(II) complexes and bis(O,O′-disubstituted phosphorodithioato-*S,S′*)nickel(II) complexes,[1] is a further confirmation that the substituent at the ligand in the plane plays an important role on the kinetics of square-planar–octahedral interconversion of nickel(II) complexes. The equilibrium constants K_{bpy}, which are expressed as the ratio between forward and reverse rate constants ($K_{bpy} = k_f/k_r$), are obviously more sensitive to the change in the nature of the substituent X. Thus, the replacement of an isopropyl group with a methyl group increases the stability constant K_{bpy} by over 20-fold, in spite of the remoteness of the substituent from the coordination center. The equilibrium constants of the reactions studied here are too large to be measured with accuracy; a direct comparison between the values of K_{bpy} evaluated kinetically as the ratio k_f/k_r and those obtained independently by other experimental means is therefore impossible. Nevertheless, an indication of the consistency of the equilibrium constants quoted in Table I can come from the comparison of the values of K_{bpy} for reaction 1 with those of K_{py} referring to the reaction of the same substrates with pyridine under the same experimental conditions (Figure 1). The values of K_{py} could be determined by calorimetry[10] or spectrophotometry.

A quantitative estimation of the substituent effect on the rate constants for reaction 1 can be made on the basis of Taft's parameters σ^*,[16] by plotting the logarithm of the rate constant for a xanthate with a given substituent against the $\sum\sigma^*$ values of the substituent itself. Such a plot, for both forward and reverse paths of reaction 1, is shown in Figure 2. It can be seen that alkyl groups, which can exert only inductive effects, lie on roughly straight lines. By converse, allyl and benzyl groups exhibit large deviations from linearity and lead to values of rate constants, k_f and k_r, respectively lower and higher than expected on the basis of Taft polar substituent constants. This deviant behavior can be accounted for in terms of stacking interactions[17] between the unsaturated allyl and benzyl groups and the aromatic rings of 2,2′-bipyridine;[18] resonance effects, which the allyl group is able to exert, can be an additional source of deviation.

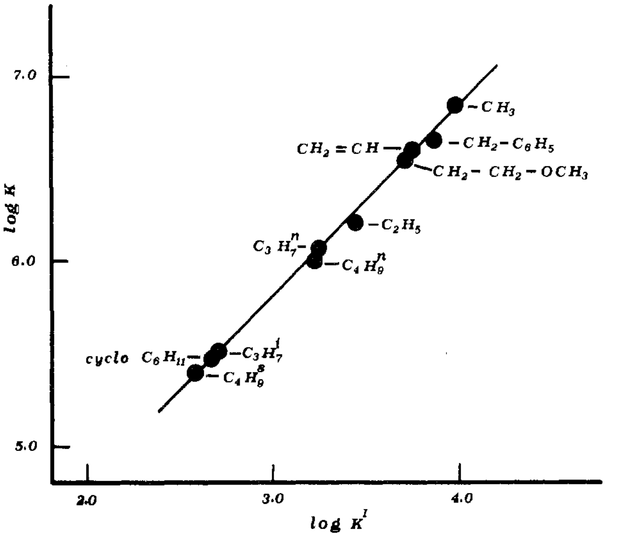


Figure 1. Plot of log K_{bpy} for reaction 1 against log K_{py} for reaction 6.

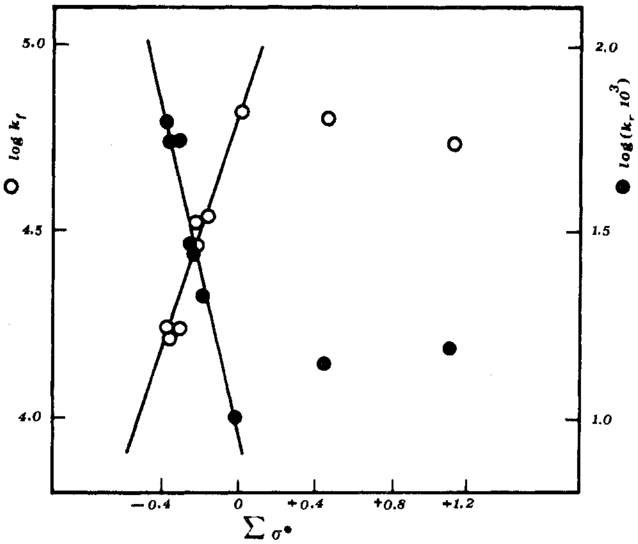


Figure 2. Relationship between Taft polar substituents constants, $\sum\sigma^*$, and forward, k_f, and reverse, k_r, rate constants for reaction 1 in benzene at 25 °C.

The nature of the processes is reflected in the values of activation parameters for reaction 5. Thus, a low activation enthalpy and a highly negative entropy are associated with the direct path, while conversely a high activation enthalpy, together with a largely positive entropy, is found for the dissociative step (see Table II). The values of the activation parameters reported here are similar to those found for analogous reactions on nickel(II) substrates,[1,2] when steric factors were absent.

Finally, the rate constants k_f for some of the reactions studied have been compared with those referring to the reaction of 1,10-phenanthroline with the analogous bis(*O,O′*-dialkylphosphorodithioato-*S,S′*)nickel(II) complexes in toluene[1]

$$\mathrm{Ni[(RO)_2PS_2]_2 + phen \overset{k_f^I}{\rightleftharpoons} Ni[(RO)_2PS_2]_2{\cdot}phen} \quad (8)$$

Such a comparison is interesting in that these two sets of square-planar complexes both have the nickel atom coordinated to four coplanar sulfur atoms. The difference in the medium of reaction, one being benzene and the other toluene, should not affect the comparison of the kinetic behavior exhibited by the two types of compounds, in that, as pointed out by Grant,[19] the solvent plays a minor role in these reactions.

Figure 3 reports the plot of the values of log k_f against those of log k_f^I; the two sets of values are correlated through the LFER

$$\log k_f = 0.37 + 0.94 \log k_f^I \quad (9)$$

The values of the slope close to unity indicate that the change

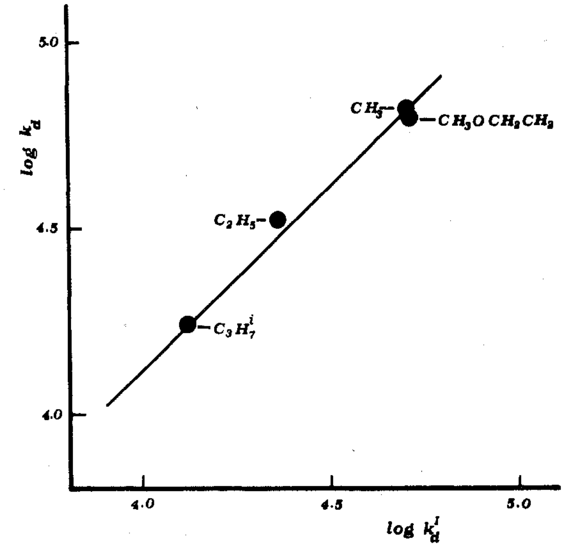


Figure 3. Plot of log k_f for reaction 1 against log k_f^I for reaction 8.

in the nature of the substituent R on the ligands $(RO)_2PS_2^-$ and $ROCS_2^-$ is relfected to the same extent in the variation of the rate constants for reaction 1 and reaction 8. This is an interesting point in that the ligand phosphorodithioate bears two substituents R while the ligand xanthate bears only one. Therefore, the effect of the substituent R is better exerted in the nickel xanthate complexes. In other words, inductive and, to a lower extent, mesomeric effects are better transmitted through the xanthate skeleton than they are through that of phosphorodithioate.

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Registry No. Ni(methyl xanthate)$_2$ (complex form), 52152-08-6; Ni(ethyl xanthate)$_2$ (complex form), 21375-69-9; Ni(*n*-propyl xanthate)$_2$ (complex form), 52139-57-8; Ni(isopropyl xanthate)$_2$ (complex form), 52057-73-5; Ni(*n*-butyl xanthate)$_2$ (complex form), 52139-58-9; Ni(*sec*-butyl xanthate)$_2$ (complex form), 71582-36-0; Ni(benzyl xanthate)$_2$ (complex form), 53566-80-6; Ni(allyl xanthate)$_2$ (complex form), 71582-37-1; Ni(methoxyethyl xanthate)$_2$ (complex form), 71582-38-2; Ni(2,6-dimethylphenyl xanthate)$_2$ (complex form), 66539-49-9; Ni(cyclohexyl xanthate)$_2$ (complex form), 53566-81-7; Ni(methyl xanthate)$_2$(bpy), 71582-39-3; Ni(ethyl xanthate)$_2$(bpy), 29827-24-5; Ni(*n*-propyl xanthate)$_2$(bpy), 71597-04-1; Ni(isopropyl xanthate)$_2$(bpy), 71582-40-6; Ni(*n*-butyl xanthate)$_2$(bpy), 71582-41-7; Ni(*sec*-butyl xanthate)$_2$(bpy), 71582-42-8; Ni(benzyl xanthate)$_2$(bpy), 71582-43-9; Ni(cyclohexyl xanthate)$_2$(bpy), 71582-44-0; Ni(allyl xanthate)$_2$(bpy), 71582-45-1; Ni(methoxyethyl xanthate)$_2$(bpy), 71582-46-2; Ni(2,6-dimethylphenyl xanthate)$_2$(bpy), 71606-76-3; bpy, 366-18-7; Ni(*n*-butyl xanthate)$_2$(py)$_2$, 71629-33-9; Ni(*sec*-butyl xanthate)$_2$(py)$_2$, 71597-49-4; Ni(allyl xanthate)$_2$(py)$_2$, 71597-50-7; Ni(methoxyethyl xanthate)$_2$(py)$_2$, 57739-18-1; Ni(methyl xanthate)$_2$ (salt form), 3427-49-4; Ni(ethyl xanthate)$_2$ (salt form), 3269-24-7; Ni(*n*-propyl xanthate)$_2$ (salt form), 5573-88-6; Ni(isopropyl xanthate)$_2$ (salt form), 3882-73-3; Ni(*n*-butyl xanthate)$_2$ (salt form), 16839-24-0; Ni(*sec*-butyl xanthate)$_2$ (salt form), 71565-82-7; Ni(benzyl xanthate)$_2$ (salt form), 68992-49-4; Ni(allyl xanthate)$_2$ (salt form), 71565-79-2; Ni(methoxyethyl xanthate)$_2$ (salt form), 71565-80-5; Ni(2,6-dimethylphenyl xanthate)$_2$ (salt form), 66367-47-3; Ni(cyclohexyl xanthate)$_2$ (salt form), 71565-81-6.

Supplementary Material Available: Listings of observed rate constants for reactions 1 and 3 (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Grant, M. W.; Magee, R. J. *Aust. J. Chem.* **1976**, *29*, 749. (b) Fayyaz, M. U.; Grant, M. W. *Ibid.* **1977**, *30*, 285. (c) Fayyaz, M. U.; Grant, M. W. *Ibid.* **1978**, *31*, 1439.
(2) (a) Cusumano, M. *J. Chem. Soc., Dalton Trans.* **1976**, 2133. (b) Cusumano, M. *Ibid.* **1976**, 2137.
(3) Shiro, M.; Fernando, Q. *Chem. Commun.* **1971**, 350.
(4) Carlin, R. L.; Siegel, A. E. *Inorg. Chem.* **1970**, *9*, 1587.
(5) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233.
(6) Fackler, J. P., Jr.; Schussler, D. P.; Chen, H. W. *Synth. React. Inorg. Met.-Org. Chem.* **1978**, *8*, 27.
(7) Sacconi, L.; Lombardo, G.; Paoletti, P. *J. Chem. Soc.* **1958**, 848.
(8) Crooks, J. E.; Tregloan, P. A.; Zetter, M. S. *J. Phys. E* **1970**, 73.
(9) In each case the spectral variation was the same as that observed on mixing equimolar amounts of Ni(Xxan)$_2$ and 2,2′-bipyridine.
(10) Graddon, D. P.; Prakash, S. *Aust. J. Chem.* **1973**, *26*, 2099.
(11) Barlin, G. B.; Perrin, D. D. "Elucidation of Organic Structures by Physical and Chemical Methods"; Bentley, K. W., Kirby, G. W., Eds.; Wiley: New York, 1972; Part I, p 611.
(12) Side experiments have shown that the reaction between Zn(Xxan)$_2$ and bipyridine, even in a ratio of 1:1, is complete within the mixing time of the stopped flow used (2 ms).
(13) Chattopadhyay, P. K.; Kratochvil, D. *Inorg. Chem.* **1976**, *15*, 3104.
(14) Kluiber, R. W.; Kukla, R.; Horrocks, W. D., Jr. *Inorg. Chem.* **1970**, *9*, 1319.
(15) Kluiber, R. W.; Thaller, F.; Low, R. A.; Horrocks, W. D., Jr. *Inorg. Chem.* **1970**, *9*, 2592.
(16) Taft, R. W., Jr. "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956, p 619.
(17) We thank a reviewer for suggesting the possibility of this effect.
(18) Cayley, G. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1974**, 1002.
(19) Sachinidis, J.; Grant, M. W. *J. Chem. Soc., Chem. Commun.* **1978**, 158.

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Dinitrogen Complexes of Iridium. Influence of Ancillary Ligands

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The comparison of synthetic, reactivity, and bonding properties of dinitrogen and carbon monoxide as isoelectronic ligands in transition metal complexes has been of interest for many years.[1] The effect of ancillary ligands on the properties of metal carbonyls has been extensively studied, but similar effects on metal–dinitrogen complexes have not been widely investigated because of their limited stabilities. The range of dinitrogen complexes of Ir(I), *trans*-$[Ir(PR_3)_2(N_2)X]$, isolated thus far is limited to $PR_3 = PPh_3$ and X = Cl,[2] Br,[3,4] or N_3.[3] Spectral evidence for the formation of complexes with X = Cl and $PR_3 = PEtPh_2$, $PBuPh_2$, PMe_2Ph, or PEt_2Ph and X = I and $PR_3 = PPh_3$ has been previously reported.[3] We have examined iridium–dinitrogen complexes prepared by reaction 1[2] for a variety of substituted phosphines, triphenylarsine, and

$$trans\text{-}[Ir(PR_3)_2(CO)X] + R'N_3 \rightarrow trans\text{-}[Ir(PR_3)_2(N_2)X] + R'NCO \quad (1)$$

anions X. Dinitrogen as a ligand for Ir(I) appears to be particularly sensitive to the electronic and steric properties of other ligands in the complex. The reasons for the lower stabilities of dinitrogen–iridium(I) complexes with other ligands have not yet been explained. To elucidate features which contribute to the stability and difficulty in isolability of dinitrogen–iridium(I) complexes, we have conducted an extensive study of reaction 1 using a variety of ancillary ligands. In the course of these studies we have isolated four new iridium–dinitrogen complexes including the first dinitrogen–iridium complex containing triphenylarsine and obtained IR data which indicate that ancillary ligands affect the CO and N_2 stretching frequencies in a similar fashion.

Experimental Section

The synthesis and characterization of the carbonyliridium(1) complexes *trans*-$[IrL_2(CO)X]$ have been described previously.[5] The purity of the complexes were ascertained by noting the absence of extraneous IR absorption bands in the 2000–2200-cm^{-1} region where

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