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N-Pyrrolyl Phosphines: Enhanced *π*-Acceptor Character *via* Carboalkoxy Substitution

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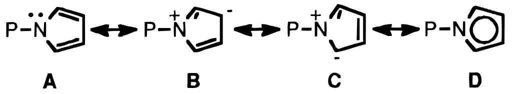
A series of 3,4-dicarboethoxy-*N*-pyrrolyl phosphine ligands ($R_2P{-}NC_4H_2(CO_2Et)_2$) is described. A number of techniques, including reaction calorimetry, infrared spectroscopy, and X-ray crystallography, demonstrate that these ligands are potent π-acceptors and that the electronic substituent parameter χ_i for the 3,4-$(EtO_2C)_2C_4H_2N$ moiety is *ca.* 16, placing it in a position between fluorine and chlorine.

Introduction

We recently reported the results of several investigations on the coordination chemistry of *N*-pyrrolyl phosphines.[1] A variety of spectroscopic, structural, and thermochemical measurements showed that these ligands are exceptional π-acceptor ligands. Our rational for this π-acceptor character is best demonstrated by resonance forms **A**−**D**. Aromatic delocalization of the nitrogen lone pair into the five-membered ring places a partial positive charge adjacent to phosphorus in contributions **B** and **C** and would be expected to render the pyrrolyl substituent an effective electron-withdrawing group. Relative to phenyl, resonance form **D** would also be expected to contribute in an electron-withdrawing fashion, since a more electronegative nitrogen atom replaces carbon.



The cumulative evidence, resulting from spectroscopic (IR) and calorimetric investigations, demonstrates that the substituent parameter χ_i for the *N*-pyrrolyl functionality is approximately 12.[1] The π-acceptor character of these ligands is thus found to exceed that of phosphites ($-OPh$, $\chi_i = 9.7$) and fluorinated aromatic phosphines ($-C_6F_5$, $\chi_i = 11.2$) and approaches that found for fluoroalkylphosphines.[2] Fluoroalkylphosphines are receiving increased attention as a result of their enhanced π-acceptor and reduced σ-donor properties relative to more traditional phosphorus ligands.[3] Phosphine ligands find enormous utility in coordination chemistry, organometallic chemistry, and homogeneous catalysis,[4] and for this reason expanding the limits of donor/acceptor properties of this general class of ligands is an area of ongoing investigation. In our continued interest in this general area, we were interested in further enhancing the π-acceptor character of *N*-pyrrolyl phosphines by placing electron-withdrawing groups on the pyrrole ring. A large body of knowledge exists on the synthesis of substituted pyrroles, and thus, this represents a viable approach to a wide variety of ligands in this general class. In this contribution, we present our recent work in this area and describe the synthesis and coordination chemistry of a series of carboethoxy-substituted pyrrolyl phosphines.

Results and Discussion

The ligands in this study are readily synthesized by direct combination of 3,4-bis(carboethoxy)pyrrole with the appropriate phosphorus chloride, as described previously for the parent ligand series (eq 1).[1a] These reactions proceed cleanly and in high yields; procedures and spectroscopic details are provided in the Experimental Section. Following this methodology, we pre-

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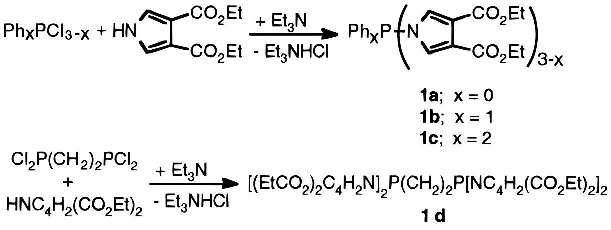

(1)

pared the series of monophosphorus ligands **1a**–**c** and the chelate **1d**, all from readily available starting materials.

These ligands form coordination complexes by simple displacement of CO from the appropriate metal carbonyl precursors. Following on our previous studies, we prepared the series of rhodium complexes **2a**–**c** *via* CO substitution and bridge cleavage from dimeric [RhCl(CO)$_2$]$_2$. Complexes **2b** and **2c** are isolable as microcrystalline solids. Complex **2a**, however, could not be isolated and was characterized *in situ*. The available evidence shows that **2a** loses a CO ligand upon attempted isolation and in this way is reminiscent of the chemistry of the complexes [R$_2$P(CH$_2$)$_2$PR$_2$]RhCl(CO). The latter lose CO to yield complexes of the type {[R$_2$P(CH$_2$)$_2$PR$_2$]RhCl}$_2$ when R is strongly electron withdrawing (R = fluoroalkyl,[3a] *N*-pyrrolyl[1a]), indicating that formation of chlorine bridges becomes more favorable as the number of π-acceptor ligands about rhodium increases. The molybdenum complex Mo(CO)$_4$(**1d**), **2d**, is readily prepared by direct reaction of the chelate with Mo(CO)$_6$ in refluxing THF.

$$[RhCl(CO)_2]_2 + 4\ PR_3 \longrightarrow 2\ \textit{trans}\text{-}RhCl(CO)(PR_3)_2 + 2\ CO$$

2a; PR$_3$ = **1a**
2b; PR$_3$ = **1b**
2c; PR$_3$ = **1c**

$$Mo(CO)_6 + \mathbf{1d} \longrightarrow Mo(CO)_4(\mathbf{1d}) + 2\ CO$$

2d

The infrared spectra of complexes **2a**–**d** demonstrate that carboalkoxy substitution on the pyrrole ring indeed results in a potent electron-withdrawing combination (see Table 1). The carbonyl stretching frequency for complex **2a** is found at 2044 cm^{-1}, 20 cm^{-1} higher than that found for the parent complex *trans*-RhCl(CO)[P(NC$_4$H$_4$)$_3$]$_2$ and 66 cm^{-1} higher than the PPh$_3$ analogue. Examination of Table 1 shows that substitution of Ph with NC$_4$H$_2$(CO$_2$Et)$_2$ in the series **2a**–**c** results in a steady 22 cm^{-1} increase in the carbonyl stretching frequency. From these data, we estimate the substituent parameter for the NC$_4$H$_2$(CO$_2$Et)$_2$ group to be *ca.* 16, placing it between chlorine ($\chi_i = 14.8$) and fluorine ($\chi_i = 18.2$) but still less than a fluoroalkyl such as CF$_3$ ($\chi_i = 19.6$).[2] That ligands **1a**–**d** fall short of the acceptor character of fluoroalkylphosphines is shown by a comparison of the molybdenum complexes Mo(CO)$_4$L; the A$_1$ band for complex **2d** is 10 cm^{-1} lower in energy than that found for the (C$_2$F$_5$)$_2$P(CH$_2$)$_2$(C$_2$F$_5$)$_2$ analogue (Table 1, entries 13 and 16).

Also included in Table 1 are the enthalpies ($-\Delta H_{rxn}$) for reaction of [RhCl(CO)$_2$]$_2$ with the new ligands to give complexes **2a**–**c**, as determined by anaerobic solution calorimetry. We previously reported a complete study of the thermodynamics of ligand substitution in this system with a number of other phosphine ligands, including the parent *N*-pyrrolyl series, and much of this data are included in Table 1 for comparison.[1c] The thermodynamic data encompass a >50 kcal/mol range and correlate nicely with the infrared data, as shown in Figure 1. The good correlation between the infrared and thermochemical data suggests that, sterically, the 3,4-disubstituted pyrrolyl group does not appear to be significantly different than the parent unsubstituted *N*-pyrrolyl. *N*-pyrrolyl, in turn, was shown in our previous studies to be isosteric with phenyl and *para*-substituted aryl groups. This is likely a result of both the remoteness of the carboethoxy groups to the coordination center and the manner in which the pyrrolyl ring directs these substituents away from the metal.

Table 1. Metal–Carbonyl Stretching Frequencies for Rh(I) and Mo(0) Complexes

entry	ligand	ν_{CO} (cm^{-1})	$-\Delta H$ (kcal/mol)[b]	ref
	trans-RhCl(CO)L$_2$[a]			
1	**1a**	2044	6.9	this work
2	**1b**	2022	23.5	
3	**1c**	2001	38.8	
4	P(pyrrolyl)$_3$	2024	34.4	1c
5	PPh(pyrrolyl)$_2$	2007	35.3	
6	PPh$_2$(pyrrolyl)	1990	43.8	
7	P(p-ClC$_6$H$_4$)$_3$	1984	47.8	
8	P(p-FC$_6$H$_4$)$_3$	1982	50.1	
9	PPh$_3$	1978	51.7	
10	P(p-CH$_3$C$_6$H$_4$)$_3$	1975	56.1	
11	P(p-OCH$_3$C$_6$H$_4$)$_3$	1973	58.7	
12	P(OPh$_3$)$_3$	2016	42.6	
	Mo(CO)$_4$(P$^\frown$P)[c]			
13	**1d**	2052[d]		this work
14	(pyrrolyl)$_2$P(CH$_2$)$_2$(pyrrolyl)$_2$	2043[e]		1a
15	(C$_6$F$_5$)$_2$P(CH$_2$)$_2$(C$_6$F$_5$)$_2$	2041[e]		3c
16	(C$_2$F$_5$)$_2$P(CH$_2$)$_2$(C$_2$F$_5$)$_2$	2064[e]		
17	Ph$_2$P(CH$_2$)$_2$PPh$_2$	2020[e]		

[a] CH$_2$Cl$_2$. [b]Enthalpy values are reported with 95% confidence limits. [c] Only the high-frequency, A$_1$ symmetry band for these C_{2v} complexes is listed; spectra for the Mo(0) complexes recorded as Nujol mulls. [d] THF. [e] Nujol mull.

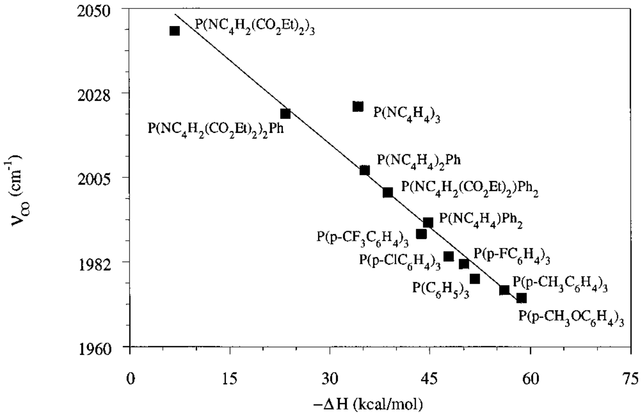

Figure 1. Carbonyl stretching frequency *vs* enthalpy of reaction for the *trans*-RhCl(CO)(PR$_3$)$_2$ system.

These inferences regarding the relative steric sizes are consistent with the structure of complex **2d**, as determined by X-ray diffraction. An ORTEP drawing of the molecule is provided in Figure 2, and important bond lengths and angles are summarized in Table 2. The structural parameters are unremarkable when compared to the structure of Mo(CO)$_4$[Ph$_2$P(CH$_2$)$_2$PPh$_2$].[5] The chelate bite angle is *ca.* 78°, as expected. Other angles about molybdenum are not chemically

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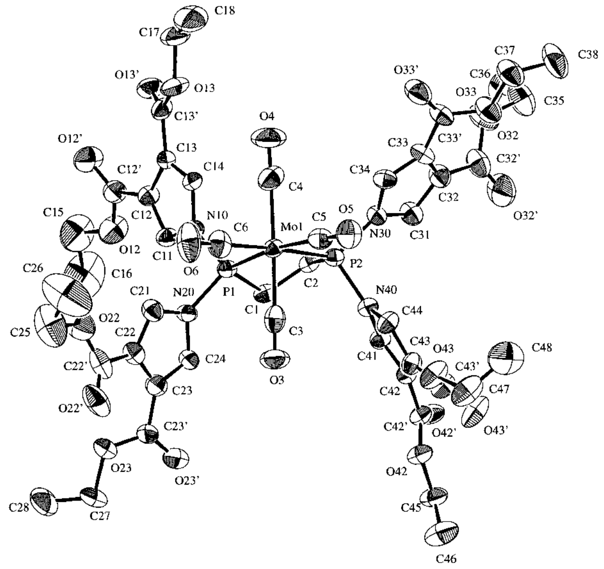
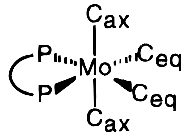


Figure 2. ORTEP drawing of complex **2d** (molecule 1); ellipsoids are drawn at the 40% probability level, and hydrogen atoms eliminated for clarity. Important bond distances and angles are provided in Table 2.

Table 2. Summary of Important Bond Distances and Angles for Complexes 2d



	2d		$Mo(CO)_4[Ph_2P(CH_2)_2PPh_2]$[a]
	molecule 1	molecule 2	
Bond Lengths (Å)			
Mo−P	2.457(2)	2.471(2)	2.500(2)
	2.430(2)	2.447(2)	2.495(2)
Mo−C_{eq}	2.004(7)	2.034(8)	1.999(8)
	2.012(8)	1.992(9)	1.974(8)
Mo−C_{ax}	2.050(8)	2.039(8)	2.053(9)
	2.021(8)	2.017(9)	2.030(9)
Bond Angles (deg)			
P−Mo−P	78.76(5)	77.77(5)	80.2(1)
C_{eq}−Mo−C_{eq}	92.2(3)	91.4(3)	90.4(3)
C_{ax}−Mo−C_{ax}	177.2(3)	171.0(4)	176.6(3)
Averages (deg)			
trans-P−Mo−C_{eq}	172.3(3)	171.0(3)	171.4(4)
cis-P−Mo−C_{eq}	94.4(3)	95.5(3)	96.4(4)
P−Mo−C_{ax}	91.1(4)	93.4(5)	88.9(4)
C_{eq}−Mo−C_{ax}	89.1(6)	87.0(8)	91.0(6)

[a] From ref 5.

different from those found in the analogous $Ph_2P(CH_2)_2PPh_2$ complex, attesting to the minimal steric impact of the 3,4-dicarboethoxy groups. The only bonding parameter of note is the Mo−P distance, which is slightly shorter (*ca.* 0.05 Å) in **2d** than that found in the $Ph_2P(CH_2)_2PPh_2$ complex. This is consistent with the greater degree of π-acceptor character of **1d** relative to $Ph_2P(CH_2)_2PPh_2$, as we previously found for complexes of P(pyrrolyl)$_3$.[1a]

Conclusion

Placement of strongly electron-withdrawing carboethoxy groups on *N*-pyrrolyl phosphines leads to a significant enhancement in the π-acceptor character of this class of ligands. The available evidence indicates that this class of phosphorus substituents is exceeded only by fluoroalkyl in terms of electron-withdrawing ability. The simple, high-yield syntheses of these ligands and the ready availability of starting materials suggests that they promise general utility as ancillary ligands in coordination chemistry, particularly when π-acceptor, "CO-like" ligands are desired.

Experimental Section

General Considerations. All manipulations were carried out under inert atmosphere using a glovebox or Schlenk line. For synthetic reactions, solvents were purchased from Aldrich as anhydrous grade and used as received; the solvent used for calorimetry was dried and distilled before use.[6−8] Deuterated solvents were dried over the appropriate agents and vacuum transferred.[6] 3,4-$(EtO_2C)_2C_4H_2NH$, PCl_3, $PhPCl_2$, Ph_2PCl, and $Cl_2PCH_2CH_2PCl_2$ were obtained from Aldrich or Strem and used as received. Et_3N was dried over molecular sieves before use.

Proton and phosphorus NMR spectra were recorded on 300 and 500 MHz instruments. The ^1H spectra are referenced to TMS *via* solvent peaks, and the ^{31}P spectra are referenced externally to 85% phosphoric acid. Infrared spectra were recorded on a Nicolet 205 FTIR spectrometer as solutions or Nujol mulls with CaF_2 cells or plates. Elemental analyses were performed by Micro-Analysis Inc., Wilmington, DE.

$P[NC_4H_2(CO_2CH_2CH_3)_2]_3$ (1a). A Schlenk flask was charged with 1.04 g (4.93 mmol) of $HNC_4H_2(CO_2CH_2CH_3)_2$ and 25 mL of THF. The solution was cooled to −30 °C, and then 0.13 mL (1.49 mmol) of PCl_3 was added, followed by 1.5 mL of Et_3N. After 15 min, the mixture was warmed to room temperature, whereupon a large amount of colorless solid formed. The mixture was heated with an oil bath at 60 °C for 6 h. After the reaction mixture was cooled to room temperature and filtered, the solids were washed with THF. The combined filtrates were taken to dryness under vacuum to yield a colorless oil. Addition of pentane caused the oil to crystallize. The product was filtered, washed with additional pentane, and dried under vacuum. Yield: 0.88 g, 90%. ^1H NMR (CD_2Cl_2): δ 1.31 (t, 18H), 4.27 (q, 12H), 7.33 (d, 6H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 82.5.

$PPh[NC_4H_2(CO_2CH_2CH_3)_2]_2$ (1b). This compound was prepared similarly, using $PPhCl_2$ (0.5 mL, 3.8 mol), $HNC_4H_2(CO_2CH_2CH_3)_2$ (2.0 g, 9.48 mmol), Et_3N (1.5 mL), and 30 mL THF. After 5 h at 60 °C, the slurry was filtered and the solids were washed with THF. The combined filtrates were taken to dryness, and the resulting product was slurried into pentane. After filtration and further washing with pentane, the colorless product was dried under vacuum: mp 129−132 °C. Yield: 1.89 g, 94%. ^1H NMR (CD_2Cl_2): δ 1.30 (t, 12H), 4.25 (q, 8H), 7.23 (m, 2H), 7.43 (d, 4H), 7.55 (m, 3H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 81.7.

$PPh_2[NC_4H_2(CO_2CH_2CH_3)_2]$ (1c). This material was prepared similarly from Ph_2PCl (0.71 mL, 3.95 mmol), $HNC_4H_2(CO_2CH_2CH_3)_2$ (1.0 g, 4.74 mmol), and Et_3N (0.66 mL, 4.74 mmol) in 15 mL of THF. Conversion to the desired product was complete after stirring overnight at room temperature. The solvent was stripped from the colorless slurry in vacuo and replaced with 15 mL of toluene. The slurry was filtered and the colorless solid was washed with toluene. The combined filtrates were taken to dryness. The resulting colorless solid was slurried into a mixture of toluene (1 mL) and pentane (10 mL), filtered, and then washed with pentane before drying under vacuum. Yield: 1.252 g, 80%. ^1H NMR (CD_2Cl_2): δ 7.47 (m, 6H), 7.33 (m, 6H), 4.25 (q, 4H), 1.30 (t, 6H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 87.1.

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$[(CH_3CH_2O_2C)C_4H_2N]_2P(CH_2)_2P[NC_4H_2(CO_2CH_2CH_3)_2]_2$ (1d). A Schlenk flask was charged with 2.05 g (9.71 mmol) of $HNC_4H_2(CO_2CH_2CH_3)_2$ and 30 mL of THF. $Cl_2P(CH_2)_2PCl_2$ (0.51 g, 2.19 mmol) was added; this was followed by 2.0 mL of Et_3N, resulting in formation of a copious, colorless precipitate. The mixture was heated to 60 °C for ca. 15 h. The ^{31}P NMR spectrum showed a single resonance at δ 77.9 assigned to the title compound. The solution was filtered, and the solvent was removed under vacuum. the resulting crude product was extracted three times with 30 mL portions of hot toluene to give a colorless solid, which was dried under vacuum: mp 139−149 °C, dec. Yield: 1.27 g, 62%. An additional 0.48 g of material was recovered from the toluene extracts (total yield = 86%). ^1H NMR (CD_2Cl_2): δ 1.29 (t, 24 H), 2.58 (t, 4 H), 4.24 (q, 16H), 7.49 (m, 8H).

$RhCl(CO)(1a)_2$ (2a). A solution of 0.145 g (0.219 mmol) of **1a** in 1 mL of CH_2Cl_2 was added to 0.0204 g (0.105 mmol) of $[RhCl(CO)_2]_2$ in 0.5 mL of CH_2Cl_2. The solution turned a darker orange, and gas evolution was observed. After 25 min, IR analysis showed complete loss of $[RhCl(CO)_2]_2$ and formation of the desired product ($\nu_{CO} = 2044$ cm^{-1}, $\nu_{ester} = 1728$ cm^{-1}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C): δ 93.6 (d, $J_{Rh-P} = 195$ Hz). Attempts to isolate this product resulted in formation of a material devoid of carbonyl ligands, as determined by IR.

$RhCl(CO)[1b]_2$ (2b). $[RhCl(CO)_2]_2$ (0.018 g, 0.0473 mmol) and **1b** (0.100 g, 0.189 mmol) were dissolved in 5 mL of CH_2Cl_2, giving immediate gas evolution and a yellow solution. After 2 h, pentane (10 mL) was added to give an orange precipitate, which was filtered, washed with pentane, and dried under vacuum. ^1H NMR (CD_2Cl_2): δ 7.7−7.5 (m, 18H), 4.17 (q, 16H), 1.20 (t, 24H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 97.3 (d, $J_{Rh-P} = 165.1$ Hz). Anal. Calcd for $C_{53}H_{58}ClN_4O_{17}P_2Rh$: C, 52.04; H, 4.78; N, 4.58. Found: C, 52.12; H, 4.51; N, 4.56.

$RhCl(CO)(1c)_2$ (2c). A solution of **1c** (0.180 g, 0.45 mmol) in 5 mL of CH_2Cl_2 was added to $[RhCl(CO)_2]_2$ (0.041 g, 0.213 mmol), resulting in gas evolution and a color change from orange to yellow. After 30 min, the solvent was removed under vacuum to yield a yellow semisolid. Pentane was added to give a solid product, which was isolated by filtration, washed with pentane, and dried under vacuum. Yield: 0.125 g, 61%. ^1H NMR (CD_2Cl_2): δ 7.7−7.5 (m, 24H), 4.25 (q, 8H), 1.29 (t, 12H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 79.7 (d, $J_{Rh-P} = 143$ Hz). Anal. Calcd for $C_{45}H_{44}ClN_2O_9P_2Rh$: C, 56.47; H, 4.63; N, 2.93; Cl, 3.70. Found: C, 56.42; H, 4.72; N, 3.17; Cl, 3.41.

$Mo(CO)_4(1d)$ (2d). A mixture of $Mo(CO)_6$ (0.104 g, 0.394 mmol), 15 mL of THF, and 0.394 g of **1d** (0.427 mmol) was brought to reflux under an argon atmosphere, whereupon the colorless solution gradually turned pale yellow. After *ca.* 15 h, IR analysis showed that no $Mo(CO)_6$ remained and only bands attributable to the title complex were observed at 2052, 1974 (sh), and 1954 cm^{-1}. Ester carbonyl bands were observed at 1732 and 1714 cm^{-1}. The solvent was removed under vacuum to yield a pale yellow solid. The product was dissolved in toluene; a small amount of colorless solid was removed by filtration, and the solvent was removed under vacuum to give a glassy product. Pentane was added to give a slurry of light yellow microcrystals. The product was isolated by filtration, washed with pentane, and dried under vacuum. Yield: 0.346 g, 77%. ^1H NMR (CD_2Cl_2): δ 7.44 (s, 8H), 4.18 (q, 16H), 3.05 (m, 4H), 1.22 (t, 24 H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 149.6 (s). Anal. Calcd for $C_{46}H_{52}MoN_4O_{20}P_2$: C, 48.52; H, 4.60; N, 4.92. Found: C, 48.05; H, 4.38; N, 4.89.

Table 3. Crystallographic Data for Complex 2d

formula	$MoP_2O_{20}N_4C_{46}H_{52}$
fw	1138.82
space group	*Cc* (No. 9)
a, Å	24.212(1)
b, Å	22.029(1)
c, Å	22.692(1)
β, deg	109.94(1)
V, Å^3	11 377.2
μ(Mo Kα), cm^{-1}	3.48
temp, °C	−112
Z	8
R^a	0.043
$R_w{}^a$	0.044
no. of refined params	1313
no. of data collected	30702
no. of data unique, $I > 3\sigma$	8051
R_{merge}	0.016

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

Solution Calorimetry. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80). This calorimeter and experimental procedures for its use under inert atmosphere have been previously described.[1c,9] Experimental enthalpy data are reported with 95% confidence limits.

X-ray Structural Analysis of 2d. Details on the structural analysis of **2d** are given in Table 3 and provided as Supporting Information. The complex crystallizes with two crystallographically independent molecules per unit cell. Unit cell information: space group, *Cc* (No. 9); $a = 24.212(1)$ Å; $b = 22.029(1)$ Å; $c = 22.692(1)$ Å; $\beta = 109.94°$; $Z = 8$; $R_w = 0.044$.

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Supporting Information Available: Tables of fractional coordinates, anisotropic thermal parameters, hydrogen fixed atom coordinates, interatomic distances, interatomic angles, and intermolecular distances for **2d** (15 pages). Ordering information may be found on any masthead page.

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