Inorganic Chemistry

Synthesis and Properties of Rhenium Carbonyl Complexes of α,α′-Bis[(1-pyrenyl)pyrazol-1-yl]alkane Ligands

Daniel L. Reger,* James R. Gardinier, Perry J. Pellechia, Mark D. Smith, and Kenneth J. Brown

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

The reaction between (1-acetyl)pyrene and dimethylformamide dimethylacetal followed by condensation of the resulting product mixture with hydrazine affords 3(5)-(1-pyrenyl)pyrazole (**2**) in good yield. The easily separable bis[(1-pyrenyl)pyrazole]methane derivatives $CH_2(3\text{-}pz^{pyrene})_2$ (**3a**, pz = pyrazolyl ring) and $CH_2(3\text{-}pz^{pyrene})(5\text{-}pz^{pyrene})$ (**3b**) were prepared by metathetical reactions between pyrazole and CH_2Cl_2, while $CH(^nPr)(pz^{pyrene})_2$ (**4**) was prepared by transamination of **2** with butyraldehyde diethylacetal. Compounds **2–4** are luminescent under irradiation with UV light and have pyrenyl monomer-based emissions centered near 400 nm. Compounds **3a** and **4** each react with $Re(CO)_5Br$ in a 1:1 molar ratio to form highly insoluble complexes $Re(CO)_3Br[(pz^{pyrene})_2CH_2]$ (**5**) and $Re(CO)_3Br[(pz^{pyrene})_2CH(^nPr)]$ (**6**). Complex $Re(CO)_3Br[(pz)_2CMe_2]$ (**7**) was also prepared. X-ray structural studies of **6** show extensive π-stacking of pyrenyl groups to form two-dimensional sheets. Pulsed field gradient spin–echo NMR (PGSE-NMR) experiments show that the complexes are monomeric in tetrachloroethane. Variable-temperature, difference NOE and 2-D NMR experiments demonstrate that isomers are present in solution that differ by restricted rotation about the pyrazolyl–pyrenyl bond. The pyrenyl-based emissions centered near 400 nm are quenched by complexation to the $Re(CO)_3Br$ moiety in **5** and **6**.

Introduction

The immense interest in the development of multidentate N-heterocycles bound to pyrenyl moieties has been driven in part by the desire to incorporate the desirable electroluminescent[1] and photophysical[2] properties of the pyrene chromophore either into systems with well-known photochemistry for the purpose of studying energy transfer[3] in the resulting bichromophoric systems or into otherwise photochemically innocuous systems such as polymers.[4] In either case, the pyrenyl-containing derivatives are environmentally responsive systems with fluorescence properties that are measurably altered by the presence of species capable of interacting with the π-cloud of the annulene fluorophore, bestowing molecular detection capabilities on the resulting materials. Whereas a number of pyrenyl derivatives of bipyridine,[3c,5] phenanthroline,[5d] and terpyridine[6] are known, reports of pyrazolyl-based derivatives are scarce,[7] with two 4,5,9,10-N,N,N,N-tetra(pyrazolyl)pyrene derivatives being

* To whom correspondence should be addressed. E-mail: reger@mail.chem.sc.edu.

(1) Köhler, A.; Wilson, J. S.; Friend R. H. *Adv. Mater.* **2002**, *14*, 701. Pongs, B.; Wokrina, T.; Matejcek, S.; Buschhaus, C.; Dormann, E. *Eur. Phys. J.* **2002**, *B28*, 289 and references therein.

(2) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.

(3) (a) Del Guerzo, A.; Leroy, S.; Fages, F.; Schmehl, R. H. *Inorg. Chem.* **2002**, *41*, 359. (b) Beinhoff, M. Weigel, W.; Jurczok, M.; Rettig, W.; Modrakowski, C.; Brudgam, I.; Hartl, H.; Schluter, A. D. *Eur. J. Org. Chem.* **2001**, 3819. (c) Hissler, M.; Harriman, A.; Khatyr, A.; Ziessel, R. *Chem. Eur. J.* **1999**, *5*, 3366. (d) Wilson, G. J.; Sasse. W. H. F.; Mau, A. W.-H. *Chem. Phys. Lett.* **1996**, *250*, 583. (e) Ford, W. E.; Rodgers, M. A. J. *J. Phys. Chem.* **1992**, *96*, 2917.

(4) (a) Cardona, C. M.; Wilkes, T.; Ong, W.; Kaifer, A. E.; McCarley, T. D.; Pandey, S.; Baker, G. A.; Kane, M. N.; Baker, S. N.; Bright, F. V. *J. Phys. Chem. B* **2002**, *106*, 8649. (b) Kane, M. A.; Pandey, S.; Baker, G. A.; Perez, S. A.; Bukowski, E. J.; Hoth, D. C.; Bright, F. V. *Macromolecules* **2001**, *34*, 6831. (c) Winnik, M. A.; Bystryak, S. M.; Liu, Z.; Siddiqui, J. *Macromolecules* **1998**, *31*, 6855. (d) Albagli, D.; Bazan, G. C.; Schrock, R. R.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97*, 10211.

(5) (a) Sohna, J.-E. S.; Carrier, V.; Fages, F.; Amouyal, E. *Inorg. Chem.* **2001**, *40*, 6061. (b) Soujanya, T.; Philippon, A.; Leroy, S.; Vallier, M.; Fages, F. *J. Phys. Chem. A* **2000**, *104*, 9408. (c). Rodriguez, A. L.; Peron, G.; Duprat, C.; Vallier, M.; Foquet, E.; Fages, F. *Tetrahedron Lett.* **1998**, *39*, 1179. (d). Bonnefous, C.; Bellec, N.; Thummel, R. P. *J. Chem. Soc., Chem. Commun.* **1999**, 1243.

(6) Krass, H.; Plummer, E. A.; Hader, J. M.; Barker, P. R.; Alcock, N. W.; Pikramenou, Z.; Hannon, M. J.; Kurth, D. G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3862.

(7) (a) Jouaiti, A.; Hosseini, M. W.; Kyritsakas, N. *Eur. J. Inorg. Chem.* **2003**, 57. (b) Suzuki, K.; Ueno, K.; Senoo, A. (Canon Inc., Japan). Jpn. Kokai Tokkyo Koho JP 2003109765, 2003. (c) Ricoh Co., Ltd., Japan. Jpn. Kokai Tokkyo Koho JP 55067751, 1980. (d) Buchta, E.; Vincke, P. *Chem. Ber.* **1965**, *98*, 208.

the only known poly[(pyrazolyl)pyrene] compounds.[7a] In this contribution, the preparation and characterization of the monosubstituted 3(5)-(1-pyrenyl)pyrazole and two of its bis-(pyrazolyl)alkane derivatives are described. In addition, because other N,N′-diimine derivatives of tricarbonylrhenium are luminescent[8] and a recent report documented the use of a pyrazolato derivative as a phosphorescent dopant in organic light-emitting electrochemical devices,[9] we have prepared and studied the properties of tricarbonylrhenium complexes of the N,N′-bis[(pyrenyl)pyrazolyl]alkanes.

Experimental Section

Solvents for synthetic procedures and spectroscopic studies were dried by conventional methods and distilled under a N_2 atmosphere immediately prior to use. All manipulations involving the preparation of rhenium complexes were carried out using standard Schlenk techniques. $Re(CO)_5Br^{[10]}$ and $Me_2C(pz)_2^{[11]}$ were prepared by literature methods. All other reagents were used as received from Aldrich Chemical Co. Full experimental details for the preparation of butyraldehyde diethylacetal, 3-(dimethylamino)-1-(1-pyrenyl)-2-propen-1-one (**1**), 3(5)-(1-pyrenyl)pyrazole (**2**) by two alternative routes, α,α′-bis[(1-pyrenyl)pyrazol-1-yl]methane (**3**), bromotricarbonyl{α,α-bis[3-(1-pyrenyl)pyrazol-1-yl]methane}rhenium (**5**), and bromotricarbonyl[2,2′-bis(pyrazol-1-yl)propane]rhenium (**7**), along with characterization data for each, are provided in the Supporting Information. Silica gel (0.040−0.063 mm, 230−400 mesh) used for chromatographic separations was purchased from Fischer Scientific. Robertson Microlit Laboratories performed all elemental analyses. Melting point determinations were made on samples contained in sealed glass capillaries using an Electrothermal 9100 apparatus and are uncorrected. Infrared spectra of approximately 15 mM $C_2D_2Cl_4$ solutions of the desired compounds contained between NaBr plates were acquired with a Nicolet 5DXB FTIR spectrometer. Mass spectrometric measurements recorded in ESI-(+) mode were obtained on a Micromass Q-Tof spectrometer, whereas those performed by using direct-probe analyses were made on a VG 70S instrument. Absorption measurements were recorded with a JASCO V-530 spectrophotometer. Emission spectra were recorded using a JASCO FP-6500 spectrofluorometer. NMR spectra were recorded by using either a Varian Mercury 400 or a Varian Inova 500 instrument, as noted in the text. Chemical shifts were referenced to solvent resonances at either δ_H 7.27, δ_C 77.23 for $CDCl_3$; δ_H 5.99, δ_C 73.28 for $C_2D_2Cl_4$, or δ_H 2.05, δ_C 29.8 for acetone-d_6.

Syntheses

3(5)-(1-Pyrenyl)pyrazole, (2). Method A.[12] A solution of 0.971 g (14.2 mmol) of hydrazine monohydrogenchloride in 100 mL of distilled water was added in one portion to a hot (40 °C) solution of 4.08 g (13.6 mmol) of **1** in 100 mL of MeOH resulting in the immediate precipitation of a canary yellow solid. The resulting mixture was heated at reflux for 1 h, cooled to room temperature,

neutralized with $NaHCO_3$, and extracted with four 100-mL portions of CH_2Cl_2. The combined organic fractions were dried over $MgSO_4$ and filtered, and solvent was removed to leave a red-orange residue that was purified by column chromatography on silica gel. Silicone grease and two unidentified blue luminescent impurities with $R_f \geq$ 0.8 were removed by elution with CH_2Cl_2. The desired compound was obtained from the next two bands (blue-green and violet luminescent bands, respectively) when the eluent was changed to 2:1 CH_2Cl_2/Et_2O and then to pure Et_2O. Evaporation of the solvent from these collected bands gave 3.26 g (89% based on **1**) of the desired compound as a pale yellow-orange solid. Compound **2** is a hygroscopic colorless solid that takes on a yellow-orange hue with trace moisture. The characterization data are for samples whose elemental analyses indicated the formula **2**·$^1/_4H_2O$. No attempt was made to rigorously dry samples of **2**·$^1/_4H_2O$ as the subsequent syntheses that utilized this substance were successful. Mp: 178−180 °C. Anal. Calcd (found) for **2**·$^1/_4H_2O$: C, 83.65 (83.56); H, 4.62 (4.51); N, 10.27 (10.11). ^{13}C NMR (101.62 MHz, $CDCl_3$): 131.4, 131.1, 130.9, 128.8, 128.0, 127.8, 127.3, 127.2, 126.1, 125.4, 125.2, 125.0, 124.8, 124.6, 106.9. See Table 1 for ^1H NMR spectral data. Direct-probe MS m/z (relative intensity, %) [assignment]: 268 (100) [M]$^+$, 239 (61) [M−N_2H]$^+$, 201 (9) [$C_{16}H_9$]$^+$. UV/vis (nm, $C_2D_2Cl_4$) λ_{max} (log ϵ): 282 (4.55), 351 (4.47).

1,1′-Bis[3-(1-pyrenyl)pyrazol-1-yl]butane (4). A 100-mL round-bottomed flask fitted with a magnetic stirbar was charged with 1.3 g (4.8 mmol) of Hpz^{pyrene} (**2**), 0.35 g (2.4 mmol) of butyraldehyde diethylacetal, 2 mL of toluene, and 0.046 g (1 mol %) of p-TsOH·H_2O. A water-cooled condenser was attached to the flask, and the mixture was heated at reflux for 12 h. TLC, GC/MS, and NMR analyses revealed the main pyrene-containing components of the product mixture at this stage of a repeated experiment to be the unreacted pyrazole **2**, $^nPrCH(OEt)(pz^{pyrene})$, and a small amount (<20%) of the desired compound $CH(^nPr)(pz^{pyrene})_2$. Therefore, an additional 0.046 g (1 mol %) of p-TsOH·H_2O was added to the flask containing the product mixture, and the flask was attached to a short-path distillation apparatus. The mixture was heated to 150−160 °C for 4 h at atmospheric pressure by an external oil bath where EtOH slowly distilled. The residue was dissolved in a minimum amount of 50% CH_2Cl_2/THF, then silica gel was added, and the solvent was removed by rotary evaporation. The mixture was loaded onto a silica gel column where slow elution with CH_2Cl_2 afforded a colorless blue luminescent band (silicone grease and another unidentified impurity), followed by a pale yellow band (bright blue-green luminescence, $R_f = 0.8$) that contained the desired compound. A second, closely following, pale yellow band (blue luminescence, $R_f = 0.7$) eluted next and contained the monosubstituted derivative $^nPrCH(OEt)(pz^{pyrene})$. Direct-probe MS m/z (relative intensity, %) [assignment]: 368 (52) [M]$^+$, 323 (5) [M − OEt], 268(100) [pz^{pyrene}]$^+$, 239 (22) [pz^{pyrene} − N_2H]$^+$, 201 (8) [$C_{16}H_9$, (1-pyrenyl)]$^+$. Finally, the column was flushed with Et_2O to recover unreacted pyrazole. Evaporation of the solvent from the first pale yellow band gave 0.612 g of $CH(^nPr)(pz^{pyrene})_2$, **4** (43% yield based on butyraldehyde diethylacetal), as a fluffy, yellow solid. Mp: 89−90 °C glass transition, 110 °C liquid. Anal. Calcd (found) for $C_{42}H_{30}N_4$: C, 85.40 (84.96); H, 5.12 (4.68); N, 9.48 (9.19). ^{13}C NMR (101.62 MHz, $CDCl_3$): 152.4, 131.6, 131.3, 131.2, 129.7, 128.9, 128.8, 128.0, 127.8, 127.7, 127.6, 126.2, 125.7, 125.4, 125.1, 125.0, 108.3, 76.6, 36.5, 19.1, 13.8. See Table 1 for ^1H NMR spectral data. Direct-probe HRMS (m/z): [M]$^+$ calcd for $C_{42}H_{30}N_4$, 590.2470; found, 590.2479. Direct-probe MS m/z (relative intensity, %) [assignment]: 590 (100) [M]$^+$, 322 (52) [M − pz^{pyrene}], 307 (3) [M − pz^{pyrene}-CH_3]$^+$, 295 (20) [M − pz^{pyrene} −CH_2CH_3]$^+$, 281 (22) [CHpz^{pyrene}]$^+$, 268 (72) [pz^{pyrene}]$^+$, 239 (22) [pz^{pyrene} − N_2H]$^+$,

(8) Guerrero, J.; Piro, O. E.; Wolcan, E.; Feliz, M. R.; Ferraudi, G.; Moya, S. A. *Organometallics* **2001**, *20*, 2842.
(9) Ranjan, S.; Lin, S.-Y.; Hwang, K. C.; Chi, Y.; Ching, W. L.; Liu, C.-S.; Tao, Y.-T.; Chien, C.-H.; Peng, S.-M. Lee, G. H. *Inorg. Chem.* **2003**, *42*, 1248.
(10) Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1990**, *28*, 160.
(11) Hill, M. S.; Mahon, M. F.; McGinley, J. M. G.; Molloy, K. C. *Polyhedron* **2001**, *20*, 1995.
(12) Adapted from Pleier, A.-K.; Glas, H.; Grosche, M.; Sirsch, P.; Thiel, W. R. *Synthesis* **2001**, 55.

Table 1. Summary of Assignments of ^{1}H NMR Resonances for Some Organic (1-Pyrenyl)Pyrazolyl Derivatives

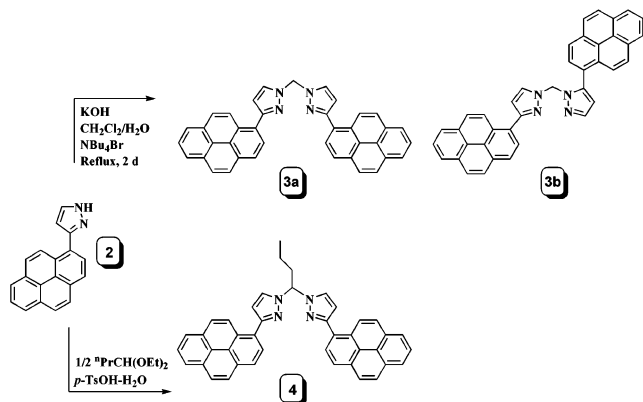| | | | pyrazolyl | | pyrenyl | | | | | | | | |
| | | | d, J = 2.5 Hz | | d, J = 7.6 Hz | | d, J = 9.0 Hz | | dd, t, dd, J = 7.6 | | | d, J = 9.3 Hz | |
compound	solvent	H$_\alpha$	H$_4$	H$_5$	H$_2$	H$_3$	H$_4$	H$_5$	H$_6$	H$_7$	H$_8$	H$_9$	H$_{10}$
H(pz^{pyrene}) (**2**)	CDCl$_3$	−	6.72	7.72	8.05	8.02	7.92	7.99	8.13	7.98	8.12	8.00	8.51
	acetone-d_6	12.75	6.84	8.09	8.31	8.28	8.17	7.99sc^a	8.29	8.07	8.27	8.19	9.13
CH$_2$(pz^{pyrene})$_2$ (**3a**)	CDCl$_3$	6.67	6.83	8.03	8.27	8.25	8.26	8.12sc^a	8.22	8.04	8.21	8.15	8.83
	acetone-d_6	6.86	6.94	8.31	8.35	8.33	8.34	8.19	8.30	8.08	8.27	8.20	9.10
CH(Pr)(pz^{pyrene})$_2$ (**4**)^b	CDCl$_3$	6.76	6.83	8.04	8.27	8.25	8.25	8.13sc^a	8.24	8.05	8.22	8.16	8.84
	acetone-d_6	7.01	6.92	8.32	8.34	8.32	8.33	8.18	8.29	8.07	8.25	8.19	9.11
	C$_2$D$_2$Cl$_4$	6.76	6.84	8.04	8.29	8.26	8.25	8.13sc^a	8.23	8.06	8.22	8.16	8.85

^{a} sc = strongly coupled, nonfirst-order system. ^{b} Propyl resonances occur with expected multiplicities at δ_H = 2.88, 1.58, 1.16 (CDCl$_3$, C$_2$D$_2$Cl$_4$) and at δ_H = 2.92, 1.57, 1.12 (acetone-d$_6$).

201 (15) [C$_{16}$H$_9$, (1-pyrenyl)]$^+$. UV/vis (nm, C$_2$D$_2$Cl$_4$) λ_{max} (log ϵ): 283 (4.90), 351 (4.84).

Bromotricarbonyl{1,1′-bis[3-(1-pyrenyl)pyrazol-1-yl]butane}-rhenium (6). A mixture of 0.090 g (0.22 mmol) of Re(CO)$_5$Br and 0.13 g (0.22 mmol) of **4** in 15 mL of toluene was heated for 5 h at reflux under N$_2$. Solvent was removed by vacuum distillation. The yellow residue was washed with two 10-mL portions of Et$_2$O, leaving a colorless solid that was dried under vacuum for 30 min. This solid was initially dissolved in 5 mL of CHCl$_3$, but within a few minutes, it precipitated (see text); the mixture was then heated to reflux and cooled to room temperature to complete the precipitation. The reprecipitated product was collected by filtration and air-dried to give 0.17 g (79%) of **6** as a colorless solid. Mp: 237−238 °C decomposition. Anal. Calcd (found) for C$_{45}$H$_{32}$N$_4$O$_4$ReBr, **6**·H$_2$O (see text): C, 56.36 (56.57); H, 3.36 (2.97); N, 5.84 (5.74). IR (C$_2$H$_2$Cl$_4$, cm^{-1}): ν_{co} 2032 (vs), 1930 (br, s), 1898 (br, s). UV/vis (nm, C$_2$H$_2$Cl$_4$) λ_{max} (log ϵ): 280 (4.90), 320 (4.43), 334 (4.76), 350 (4.90). ^{1}H NMR (400 MHz, C$_2$D$_2$Cl$_4$): 9.01 (br, s, PrCH), 8.27−7.95 (br, m, pyrenyl + H$_5$ − pz), 7.78 (d, J = 9.3 Hz), 7.75 (d, J = 9.3 Hz), 7.68 (d, J = 9.3 Hz), 6.76 (d, J = 2.5 Hz), 6.71 (d, J = 2.5 Hz), 6.70 (d, J = 2.5 Hz), 2.84 (m, CH$_2$CH$_2$CH$_3$), 1.93 and 1.85 (br, m, −CH$_2$CH$_2$CH$_3$), 1.30 (br, m, CH$_3$); see text for details. HRMS-ESI(+) (m/z): [M − Br]$^+$ calcd for C$_{45}$H$_{30}$N$_4$O$_3$-Re, 861.1878; found, 861.1885. ESI(+) MS m/z (relative intensity, %) [assignment]: 902 (3) [Re(CO)$_3$(CH$_3$CN)(L)]$^+$, 861 (100) [Re(CO)$_3$(L)]$^+$, 394 (15) [Re(CO)$_3$(CH$_3$CN)$_3$]$^+$. Direct-probe MS m/z (relative intensity, %) [assignment]: 940 (0.05) [Re(CO)$_3$-Br(L)]$^+$, 590 (10) [L]$^+$, 322 (62) [L − pz^{pyrene}]$^+$, 281 (24) [CHpz^{pyrene}]$^+$, 268 (100) [Hpz^{pyrene}]$^+$, 239 (39) [Hpz^{pyrene} − N$_2$H]$^+$, 201 (13) [C$_{16}$H$_9$]$^+$.

Crystal Structure Determination of 6. Crystals of the title compound were available only as tiny colorless needles of mediocre quality. The largest and best of these was mounted onto the end of a thin glass fiber using inert oil for data collection (see Table 2). X-ray intensity data covering the full sphere of reciprocal space

Table 2. Crystallographic Data for Re(CO)$_3$Br[(pz^{pyrene})$_2$CH(^{n}Pr)]· 0.25Et$_2$O·0.25Acetone

compound	**6**·0.25Et$_2$O·0.25 acetone
C$_{46.75}$H$_{34}$BrN$_4$O$_{3.50}$Re	formula weight, 973.89
a = 8.6491(8) Å	T = 150(1) K
b = 14.6714(13) Å	λ = 0.71073 Å
c = 17.2380(16) Å	D (calcd) = 1.649 g/cm^3
α = 66.333(2)°	μ = 4.166 mm^{-1}
β = 78.312(2)°	space group P-1
γ = 83.869(2)°	R = 0.0542
V = 1961.1(3) Å^3	R_w = 0.1225
Z = 2	

were measured at 150(1) K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, λ = 0.710 73 Å).[13] The raw data frames were integrated and corrected for Lp effects with SAINT+.[13] The final unit cell parameters are based on the least-squares refinement of 5195 reflections from the data set with I > 5$(\sigma)I$. Analysis of the data showed negligible crystal decay during data collection. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied with the program SADABS.[13]

The compound crystallizes in the triclinic system in the space group P-1. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares against F^2 with SHELXTL.[14] All atoms of the rhenium complex were refined with anisotropic displacement parameters. A region of disordered solvent situated about an inversion center was modeled as $1/4$ acetone and $1/4$ diethyl ether per rhenium complex and refined with a common fixed isotropic displacement parameter, with the aid of 16 geometric restraints. All hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.

(13) *SMART*, version 5.625; *SAINT+*, version 6.22; and *SADABS*, version 2.03; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.
(14) Sheldrick, G. M. *SHELXTL*, version 6.1; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

Scheme 1. Optimal Route to 3(5)-(1-Pyrenyl)pyrazole

Conditions: *i.* excess Me₂NCH(OMe)₂, reflux 20 h, H₂O. *ii.* H₂N-NH₃Cl, reflux 1h.

Scheme 2. Preparation of Bis[(1-pyrenyl)pyrazolyl]alkanes
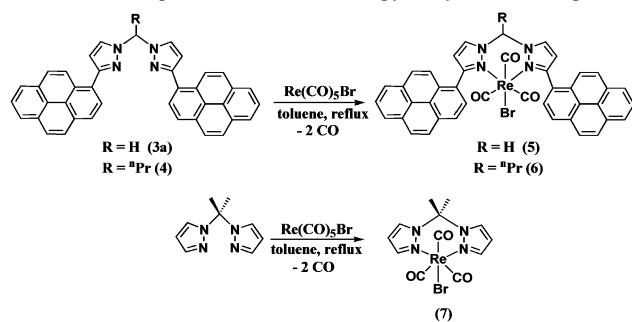

Results and Discussion

Ligand Syntheses. The reaction between (1-acetyl)pyrene and dimethylformamide dimethylacetal followed by condensation of the pyrenyl acrolein, **1**, with hydrazine monohydrogenchloride afforded the desired pyrazole, **2**, in 77% yield, as depicted in Scheme 1. A convenient feature of the first step of the depicted pathway is that, after standard hydrolytic workup, extraction, and solvent removal by rotary evaporation, an oil with the composition (pyrene)C(O)CHCH-(NMe₂)·1.5DMF (as determined by integration of its ^{1}H NMR spectrum) was isolated and could be used directly for the preparation of the desired pyrazole in good yield. Alternatively, the DMF-free intermediate (1-pyrene)C(O)-CHCH(NMe₂) was also obtained by separating the constituents of the oil on a silica gel plug and was used successfully for the preparation of **2**, although the overall yield was slightly lower than when the crude oil was used. The preparation of **2** by the more typical Claisen route (the reaction between acetylpyrene, ethyl formate, and sodium methoxide) was riddled with difficulties: The first intermediate Na[(1-pyrene)C(O)CH₂C(O)H] forms a gel at high concentrations in toluene hindering its isolation by filtration. Once obtained, this intermediate and the subsequent products exhibited low solubility in the solvents employed. Each of these experimental complications likely contributed to the lower yield of this latter route (38%) when compared to that depicted in Scheme 1.

The compounds CH₂(pz^{pyrene})₂ (**3**) and CH(^{n}Pr)(pz^{pyrene})₂ (**4**) were prepared by following established methodology for the preparation of other bis(pyrazolyl)alkanes, as depicted in Scheme 2. Thus, the biphasic metathetical reaction between CH₂Cl₂ and K(pz^{pyrene}) (formed in situ) in the presence of phase-transfer catalyst afforded a 62% yield of **3** as a mixture of 3,3- (**3a**) and 3,5- (**3b**) isomers in a 2:1 mol ratio. The isomers could be separated by column

chromatography, and the identity of each was established by using a combination of NMR spectral data (vide infra) and, in the case of **3a**, X-ray diffraction studies of the reaction product with Re(CO)₅Br (see Supporting Information). The compound CH(^{n}Pr)(pz^{pyrene})₂, **4**, was prepared by the reaction between butyraldehyde diethylacetal with 2 equiv of Hpz^{pyrene} at 150 °C. The desired product was formed in significant amounts only when ethanol was dynamically removed from the reaction mixture. Otherwise, HC(^{n}Pr)(OEt)(pz^{pyrene}) was isolated as the main product as determined from GC/mass spectra, NMR spectra, and mass measurements (of recovered pyrazole).

Ligand Characterization. NMR Spectroscopy. Each of the newly prepared (pyrenyl)pyrazole derivatives **2**, **3a**, and **4** was characterized by multiple advanced NMR spectroscopic methods not only as an attempt to provide full assignments for their ^{1}H NMR spectra but also to provide a basis for elucidating potentially challenging spectra of metal complex derivatives. Although the ^{1}H NMR spectrum of each compound was complicated as a result of numerous overlapping multiplet resonances in the low-field region, the assignments were tractable, and the results of these studies are summarized in Table 1. As expected for (1-pyrenyl)-pyrazole, four pairs of doublets, one set of multiplets (two doublets of doublets and one triplet for H₆, H₈, H₇, respectively), and a broad singlet for N−H comprise the NMR spectrum, as determined from an inspection of the normal, the homonuclear *J*-resolved, and the DQCOSY spectra. Referring to the figure in the inset of Table 1, the resonances for H₆, H₇, and H₈ are easily distinguished in the homonuclear *J*-resolved experiment as a result of their unique multiplicities. The remaining four doublets can be categorized by their coupling constants. The hydrogens of the pyrazolyl group have a coupling constant *J* = 2.5 Hz, whereas those of the pyrenyl group can be subdivided into three sets: a small (*J* = 7.6 Hz), a midrange (*J* = 9.0 Hz), and a large (*J* = 9.3 Hz) coupling constant. The NOE difference spectra of the pyrazole **2** were used to establish the relative positions of the latter three pairs of doublets about the pyrenyl ring. Selective irradiation of the resonance for H₄ of the pyrazolyl ring caused NOE enhancement to one resonance each of the small-*J* and large-*J* pair of doublets, which assigned the midrange-*J* doublet to the distal ring containing H₄ and H₅. Irradiation of the doublet of doublet resonances at ca. δ 8.13 caused NOE enhancement to one resonance of the distal ring (H₅) and to one of the resonances for the large-*J* doublet. This observation fixed the position of the small-*J* doublet to the ring with H₂ and H₃ and, hence, the position of the large-*J* doublet to the ring with H₉ and H₁₀. The NMR spectra of compounds **3** and **4** were similar but had resonances for their respective alkane backbones instead of a NH resonance. Sample spectra for each compound are provided in the Supporting Information.

Electronic Spectroscopy. The absorbance spectra of compounds **2**−**4** (Supporting Information) are typical of those for other N-heterocycles with covalently bound pyrenyl groups in that a long-wavelength absorption for a pyrenyl-based π−π* transition is found centered at 350 nm while

Complexes of α,α′-Bis[(1-pyrenyl)pyrazol-1-yl]alkane Ligands

Scheme 3. Preparation of Rhenium Bis(pyrazolyl)alkane Complexes

Figure 1. ORTEP diagram of the molecular unit of Re(CO)$_3$Br[(pz^{pyrene})$_2$-CH(^{n}Pr)] (**6**) with 50% probability ellipsoids.

the heterocyclic (pyrazolyl)-based $\pi-\pi^*$ transition is found centered near 280 nm.[15] Excitation at either of the wavelengths corresponding to the two absorption maxima produces the broad emissions centered at 406, 396, and 392 nm for compounds **2**, **3a**, and **4**, respectively. The wavelengths of these emission bands are comparable to those for pyrenyl monomer-based (380−400 nm) rather than excimer-based emissions[2] that are generally above 480 nm. These data suggest that **2**−**4** are monomeric in dilute tetrachloroethane solution, rather than being associated via intermolecular π-stacking interactions.

Rhenium Complexes. Syntheses. The rhenium derivatives of **3** and **4** and of 2,2′-bis(pyrazolyl)propane (for comparison purposes) were prepared by reacting Re(CO)$_5$Br with the appropriate ligand in a 1:1 molar ratio in toluene according to Scheme 3. Whereas compound **7** precipitates cleanly from the reaction mixture, compounds Re(CO)$_3$Br[(pz^{pyrene})$_2$CH$_2$] (**5**) and Re(CO)$_3$Br[(pz^{pyrene})$_2$CH(^{n}Pr)] (**6**) required extensive drying and reprecipitation with chloroform to liberate trace toluene. The reprecipitated products **5** and **6** exhibit moderate solubility in tetrachloroethane (heating is required to dissolve samples to maximum concentration of about 15 mM), only trace solubility in acetone, and virtually no solubility in most other common organic solvents. The IR spectrum of each compound **5**−**7** in tetrachloroethane has three bands for CO stretches as expected for a *fac*-tricarbonylrhenium. The mass spectra of compounds **5**−**7** share the following features: The parent ions [Re(CO)$_3$Br(L)]$^+$ could be seen as peaks of low intensity in the direct-probe experiments, whereas they were not observed in the ESI(+) experiments. Peaks corresponding to the loss of bromine ([Re(CO)$_3$(L)]$^+$ ions) were observed in both sets of experiments and for [Re(CO)$_3$(solvent)(L)]$^+$ in the ESI(+) experiments.

Crystallography. Crystals of **6** suitable for single-crystal X-ray diffraction analysis were grown by vapor diffusion of Et$_2$O into an acetone solution of the initial toluene precipitate from the preparative reaction. The molecular structure and atomic labeling scheme are shown in Figure 1, and selected bond lengths and angles are collected in Table 3. The first noteworthy feature regarding the structure of the compound was that the pyrenyl groups are in the expected 3-position of the pyrazolyl ring rather than being in the 5-position. This feature was also observed in the structure of Re(CO)$_3$Br-
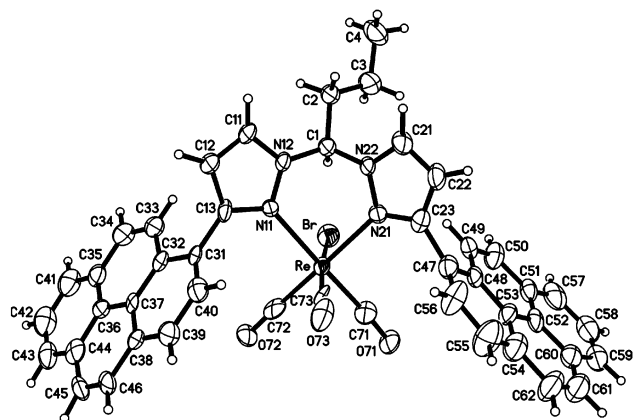
[(pz^{pyrene})$_2$CH$_2$], **5** (Supporting Information), and also assisted in the ^{1}H NMR assignments as isomers where both 1-pyrenyl substituents are in either the 3- or 5-position of the pyrazolyl rings in a bis(pyrazolyl)alkane ligand should give rise to qualitatively similar spectra (vide infra). Second, the nitrogen donors of the pyrazolyl rings occupy positions trans to two of the three facially arranged carbonyls, with the bromine occupying the remaining position. All bond distances and angles involving rhenium and its ligating donor atoms are within typical values.[16] Another feature of interest in the structure of **6** is that both bromine and H(1) occupy axial positions of the boat where their interatomic separation of 2.64 Å is less than 2.97 Å, the sum of their van der Waals radii.[17] This short CH···Br distance and the associated angle (148.9°) are representative of a weak hydrogen-bonding interaction and might contribute to the greater boatlike character of the chelate ring in **6** compared to that found in Re(CO)$_3$Br[(pz)$_2$CMe$_2$]. (See Supporting Information for a more complete comparison.) Some final features of interest are that the mean planes of the bonded pyrazolyl and pyrenyl groups are nearly orthogonal (93.1°, 96.5°) and the mean planes of each of the two pyrene rings are tilted 121.2° from one another where the bulk of the unsymmetrical plane of each 1-pyrenyl group is directed up toward bromine above the rhenium−nitrogen bonds. These features favor extensive $\pi-\pi$ stacking and CH−π interactions involving both pyrenyl and pyrazolyl groups that organize **6** into two-dimensional sheets as depicted in Figure 2. A full discussion detailing the supramolecular structure can be found in the Supporting Information. The extensive $\pi-\pi$ stacking and CH−π interactions are thought to contribute significantly to the low solubility of complexes **5** and **6**.

(15) Simon, J. S.; Curry, S. L.; Schmehl, R. H.; Schatz, T. R.; Piotrowiak, P.; Jin, X.; Thummel, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 11012.

(16) (a) Reger, D. L.; Brown, K. J.; Smith, M. D. *J. Organomet. Chem*, **2002**, *658* (1−2), 50. (b) Alves, S.; Paulo, A.; Correia, J. D. G.; Domingos, A.; Santos, I. *J. Chem. Soc., Dalton Trans.* **2002**, *24*, 4714. (c) Riklin, M.; Tran, D.; Bu, X.; Laverman, L. E.; Ford, P. C. *J. Chem. Soc., Dalton Trans.* **2001**, *12*, 1813. (d). Ardizzoia, G. A.; LaMonica, G.; Maspero, A.; Moret, M.; Masciocchi, N. *Eur. J. Inorg. Chem.* **1971**, *10*, 1503. (e) Orrell, K. G.; Osborne, A. G.; Da Silva, M. W.; Hursthouse, M. B.; Coles, S. J. *Polyhedron* **1997**, *16*, 3003. (f) Cobbledick, R. E.; Dowdell, L. R. J.; Einstein, F. W. B.; Hoyano, J. K.; Peterson, L. K. *Can. J. Chem.* **1979**, *57*, 2285.

(17) Rowland, R. S.; Taylor, R. *J. Phys. Chem.* **1996**, *100*, 738.

Table 3. Selected Bond Lengths (Å) and Angles (°) for $Re(CO)_3Br[(pz^{pyrene})_2CH(^nPr)]$ (**6**)

bond lengths			bond angles		
Re−C(73)	1.858(12)	C(73)−Re−C(72)	88.5(5)	C(72)−Re−N(11)	94.8(3)
Re−C(72)	1.883(11)	C(73)−Re−C(71)	87.9(4)	C(71)−Re−N(11)	178.3(4)
Re−C(71)	1.899(11)	C(72)−Re−C(71)	86.5(4)	N(21)−Re−N(11)	84.0(3)
Re−N(21)	2.221(7)	C(73)−Re−N(21)	90.9(4)	C(73)−Re−Br	174.1(3)
Re−N(11)	2.241(7)	C(72)−Re−N(21)	178.6(3)	C(72)−Re−Br	91.5(3)
Re−Br	2.6237(12)	C(71)−Re−N(21)	94.7(4)	C(71)−Re−Br	86.2(3)
		C(73)−Re−N(11)	93.2(4)	N(21)−Re−Br	89.3(2)
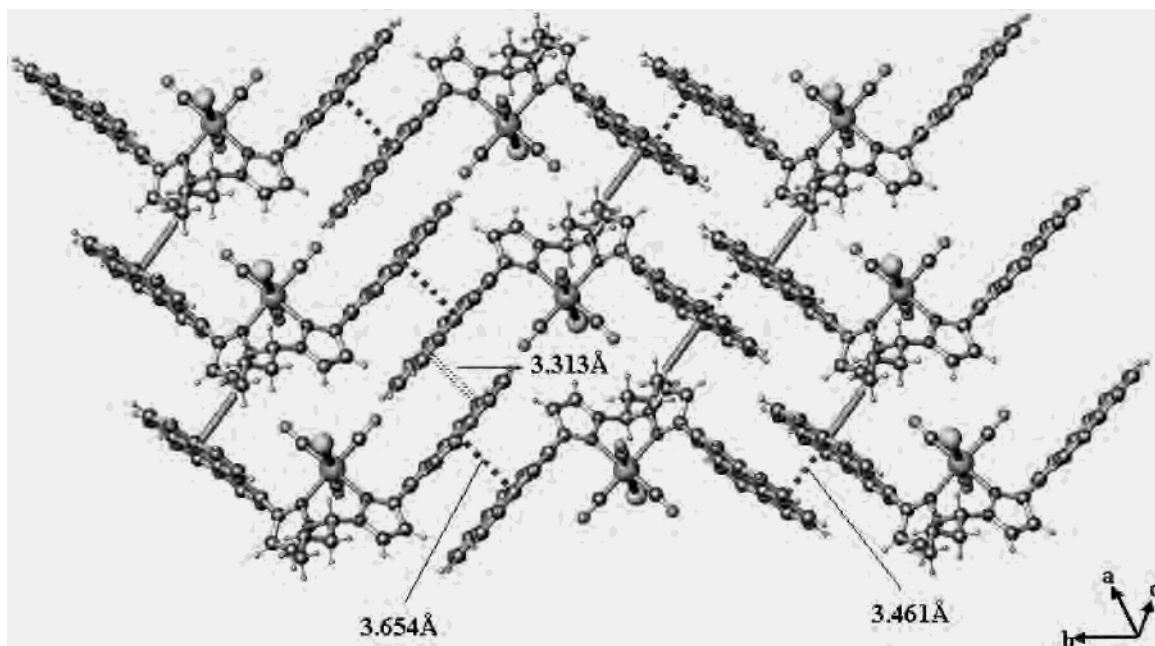
Figure 2. Two-dimensional sheet in **6** formed by CH−π (solid line) and π−π (dashed line) stacking interactions. The perpendicular interplane separation of 3.313 Å occurs between nonoverlapping pyrene centers (i.e., not a π−π interaction).

NMR Spectroscopy. Multiple NMR experiments revealed several features concerning the solution chemistry of compounds **5**−**7** that can be summarized as follows: (a) Compounds **5** and **6** exist as multiple conformational isomers in solution that are related by (restricted) rotation of the 1-pyrenyl groups. (b) Only one of a possible two geometrical isomers of compound **6** is isolated from the preparative reaction. (c) Compounds **5** and **6** begin to decompose in solution at about 120 °C, presumably to give an ionic species of the form $[Re(CO)_3(solvent)^+][Br^-]$. (d) Compounds **6** (and by analogy **5**) and **7** are monomeric in tetrachloroethane.

Figure 3 provides a comparison of the low-field regions of the room-temperature ^1H NMR spectra for **5** (top) and **6** (bottom). Because of the more extensive overlap of a larger quantity of multiplet signals in the spectra of compounds **5** and **6** compared to the spectra of the free ligands, complete assignments were not possible. Although an attempt to resolve the spectrum of **6** by titration with the shift reagent $Eu(FOD)_3$ proved unsuccessful, as might be suspected, information from DQCOSY experiments allowed the identification of several key resonances. The lowest-field resonances in each spectrum are signals from a hydrogen of the central carbon of the chelate ring. As has been observed in tris(pyrazolyl)methanerhenium complexes,[16a] when the acidic hydrogen bound to the central methine carbon participates in weak hydrogen-bonding interactions, a significant downfield shift of its resonance occurs compared to that of the
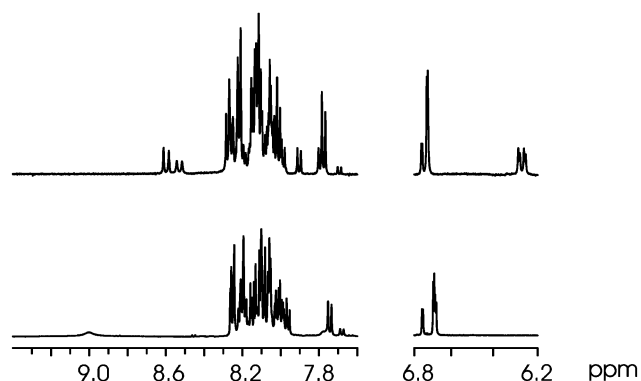
Figure 3. Low-field regions of ^1H NMR spectra of **5** (top) and **6** (bottom) in $C_2D_2Cl_4$.

free ligand. Therefore, in the case of **5**, the two doublets in the 8.6−8.5 ppm range and, in the case of **6**, the broad signal of weak intensity (actually two signals, vide infra) at ca. 9 ppm are attributed to the hydrogens occupying axial positions of the $Re(pz)_2CHR$ (R = H (**5**), ^nPr (**6**)] ring that weakly interact with the bromine. The occurrence of two sets of doublets for compound **5** is due to the presence of two isomers in which the axial hydrogen of each is coupled to the magnetically inequivalent equatorial hydrogen whose resonance occurs between 6.3 and 6.2 ppm. Interestingly, no such high-field resonance exists in the spectrum of compound **6**, indicating that only one of the two possible
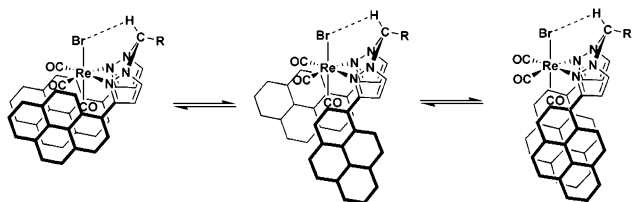
Figure 4. Proposed exchange process for **5** and **6**.

geometrical isomers is present in solution. Because compound **6** was isolated in 79% yield, it would appear that the isomer with the hydrogen of the methine carbon oriented in the direction of the bromine is preferentially formed in the preparative reaction over the isomer with the hydrogen oriented toward the axial carbonyl (and propyl group in the direction of the bromine). This rather surprising result can be justified by proposing that a weak CH···Br hydrogen-bonding interaction is involved in the transition state during the formation of **6**. In the spectra of **5** and **6**, the three high-field doublet resonances ($J = 2.5$ Hz) that occur between δ 6.8−6.6 ppm arise from the hydrogens in the 4-position of the pyrazolyl rings. The H$_5$-pyrazolyl resonances to which the H$_4$-pz resonances are coupled occur between 8.1 and 8.0 ppm, overlapping the multiple pyrenyl resonances. Finally, the doublets ($J = 9.3$ Hz) in the region between δ 7.9−7.6 ppm are assigned to the hydrogens in the 10-position of the pyrenyl rings. Four sets of these doublets are found in the spectrum of **5**, whereas only three sets are detected in the room-temperature spectrum of **6**. As will be shown, the number of resonances in the spectrum of each compound is attributed to the existence of isomers in solution. The three possible isomers that retain their C−H···Br hydrogen bonding are pictured in Figure 4, where two symmetrical isomers have the bulk of the pyrenyl groups directed either up or down in relationship to the rhenium−bromine bond and the remaining unsymmetrical isomer has one pyrene group directed up and the other directed down.

The temperature dependence of the ^{1}H NMR spectra of **5** and **6** is shown in Figure 5, indicating that the isomers equilibrate at higher temperatures. With the exception of the H$_{10}$-pyrene resonances for compound **5**, only two of the three conformational isomers have either chemical shifts that are distinct enough at any temperature or, as is likely the case in compound **6**, concentrations appreciable enough to be detected. Relative integration of the four resonances observed for the H$_{10}$-pyrenyl hydrogen atoms in the spectra of compound **5** over the temperature range 30−80 °C (where reliable integrations could be obtained) indicated that the overall percent distribution of isomers in **5** is 48% (symmetrical)/45% (unsymmetrical)/7% (symmetrical), although it is unclear which of the symmetrical isomers is predominant.

In the spectra, it should be reemphasized that, at any given temperature, the resonances for the (weakly hydrogen bonded) axial methine hydrogens are maintained for **5** and **6** throughout the temperature range, indicating that the boat structure of the chelate ring is preserved. Also, with the exceptions of the H$_{10}$-pyrenyl resonance initially at 7.9 ppm and the equatorial methine hydrogen resonances for com-
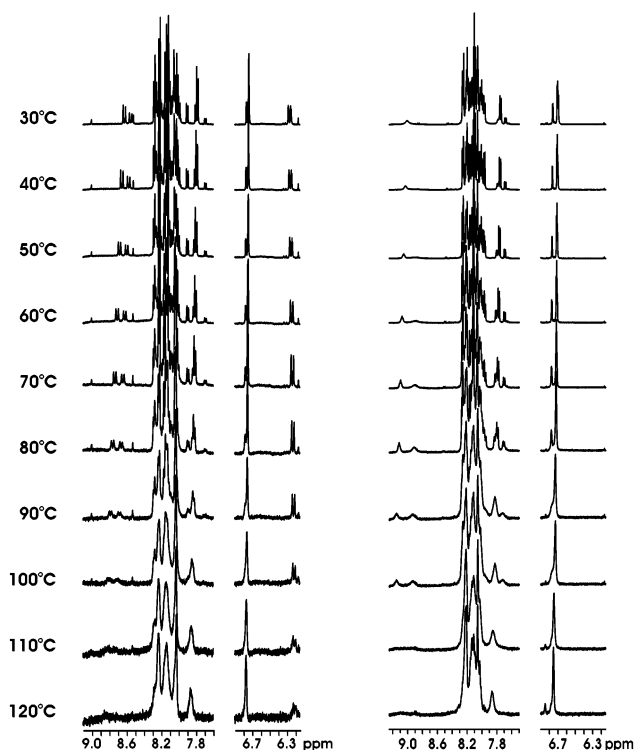

Figure 5. Variable-temperature NMR spectra of compounds **5** (left) and **6** in C$_2$D$_2$Cl$_4$.

pound **5**, the remaining assignable resonances of the bis-[(pyrenyl−pyrazolyl)]alkane ligands exhibited a downfield shift with an increase in temperature before their respective coalescence temperature; the former resonances shifted upfield. In the spectra of compound **6** between 30 and 80 °C, the broad single resonance for the methine hydrogen at 9.1 ppm sharpened along with a second resonance at 8.9 ppm, which was expected for the methine hydrogen of a second isomer (analogous to that for compound **5**) but was not initially detected at room temperature because of extensive broadening. Raising the temperature of solutions of **5** and **6** from 30 to 120 °C led to coalescence of the resonances for the axial methine, the H$_4$-pyrazolyl, and the H$_{10}$-pyrenyl hydrogens of all isomers. Over the same temperature range, the multiple overlapping pyrenyl and H$_5$-pyrazolyl resonances coalesced into four overlapping broad signals. The values of the free energy of activation for the exchange processes as measured for each resonance type are very similar, and the mean values are $\Delta G^{\ddagger} = 18.9 \pm 0.8$ and 19.1 ± 0.8 kcal/mol for **5** and **6**, respectively. These values were estimated by using the approximation for a two-site exchange (unsymmetrical to symmetrical) $\Delta G^{\ddagger} = 4.57T_c \cdot [10.32 + \log(\sqrt{2}T_c/\pi \cdot \delta\nu)]$ where T_c is the temperature (K) at which coalescence occurred between two signals that were separated by a chemical shift difference $\delta\nu$ (in Hz) in the absence of exchange.[18] The temperature dependence of each spectrum was reproducible only when samples were kept below 120 °C (and the fast exchange limit was not reached) because heating above 120 °C caused decomposition so that the low-temperature spectra were not recovered on cooling.

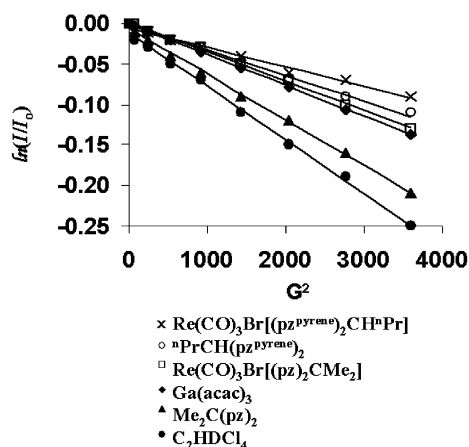(18) Kessler, H. *Angew. Chem., Int. Ed. Eng.* **1970**, 9219.

Figure 6. Results from PGSE experiments.

Table 4. Comparison of Radii Calculated from PGSE Measurements and from X-ray Data

	calculated radii (Å)	
compound	PGSE	X-ray
C_2HDCl_4	2.07[a]	na
C_2HDCl_4	2.07[a]	na
$Ga(acac)_3$	4.84	4.81[24]
$Me_2C(pz)_2$	3.20	3.87[25]
$Re(CO)_3Br[(pz)_2CMe_2]$	4.60	4.11
$CH(^nPr)(pz^{pyrene})_2$	6.23	na
$Re(CO)_3Br[(pz^{pyrene})_2CH(^nPr)]$	8.29	8.91

[a] Calculated at infinite dilution. (See Supporting Information.)

In samples heated above 120 °C, the methine and 4-pyrazolyl hydrogen resonances are replaced by new resonances at ca. δ 12 (CH) and 6.9 (H$_4$-pz) ppm. The chemical shifts of these new resonances are similar to those seen for cationic tricarbonylrhenium derivatives of tris(pyrazoly)methanes; therefore, we attribute these new resonances to species such as [LRe(CO)$_3$(solvent)$^+$][Br$^-$] similar to that detected in the mass spectral experiments.

The possibility that the association/dissociation of intermolecularly π-stacked oligomers of **5** and **6**, such as observed in the solid-state structure of **6**, was responsible for the variable-temperature NMR spectra was excluded by examining the results of pulsed-field gradient spin−echo NMR (PGSE-NMR) experiments. As has been described in detail elsewhere,[19] the PGSE-NMR technique provides an indirect measure of molecular size by allowing the determination of the diffusion coefficients of a given species in solution and applying the Stokes−Einstein expression to yield the hydrodynamic radius. This technique has been used successfully in a number of applications recently ranging from determining the size of hydrogen-bonded supramolecules[20] and inorganic macrocycles[21] to detecting the extent of agglomeration of ions in solution.[22] In the case of compound **6**, the expected difference in hydrodynamic radius of a monomeric species and that of a dimeric π-stacked unit should be appreciable and easily detectable such that the simple Stejskal−Tanner pulse sequence can be used reliably.[23] Figure 6 shows a plot of ln(I/I_o) [the logarithm of signal intensity (*I*) with respect to signal intensity in the absence of gradients (I_o)] versus the square of the gradient field strength (G^2), which are related by the expression ln(I/I_o) = $-\gamma\delta^2G^2(\Delta - \delta/3)D$, where δ is the length of gradient pulse, Δ is the midpoint between gradient pulses, γ the magnetogyric ratio, and *D* is the diffusion coefficient. Table 4 provides a comparison of experimentally determined hydrodynamic radii of some model compounds along with the title compounds with the radii calculated from crystallographic data where it was available. As can be seen, the radii obtained for the model compounds from diffusion experiments and the radii calculated from solid-state structural studies typically deviated by only 10−20%. Of particular interest was that the hydrodynamic radii of compound **6** and the pure ligand **3** were consistent with monomeric species in tetrachloroethane solution.

Electronic Spectroscopy. The absorbance spectra of compounds **5** and **6** show structured pyrenyl-based $\pi-\pi^*$ absorption bands similar to those found in other pyrenyl-containing systems[2] (Supporting Information). Both the pyrenyl-based and pyrazolyl-based $\pi-\pi^*$ absorptions show hypsochromic shifts when compared to those of the free ligands, which would be expected if the extent of conjugation between the chromophores is reduced as a result of complexation. No evidence of d$\pi-\pi^*$ MLCT bands was found in the spectra of compounds **5**−**7**.

The emission spectra of compounds **5**−**7** produced when each compound was irradiated at any of the wavelengths of light corresponding to their absorption maxima were essentially identical in that they were either only very weakly (**5** and **6**) or non- (**7**) luminescent, even in the absence of oxygen. Figure 7 provides a comparison between the emission spectra of the pyrenyl-based ligands **2**−**4** and the rhenium complexes **5**−**7** in tetrachloroethane. The complexation of Re(CO)$_3$Br units by bis[(1- pyrenyl)pyrazolyl]-alkanes causes quenching of the pyrenyl monomer fluorophores. The monomeric nature of compound **6** in tetrachloroethane shown by the NMR experiments implicates an intramolecular pathway for fluorescence quenching. Removal of the bromide by reaction with silver tetrafluoroborate failed to restore pyrenyl-based fluorescence, implicating the rhenium center as the source of fluorescence quenching.

Conclusions

We have developed an efficient synthesis of the first (1-pyrenyl)pyrazole and have converted it into two new bis-(pyrenyl)pyrazolylalkane ligands. These ligands readily react

(19) (a) Valentini, M.; Pregosin, P. S.; Rüegger, H. *Organometallics* **2000**, *19*, 2551. (b) Stilbs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1.
(20) Timmerman, P.; Weidmann, J.-L.; Jolliffe, K. A.; Prins, L. J.; Reinhoudt, D. N.; Shinkai, S.; Frish, L.; Cohen, Y. *J. Chem. Soc., Perkin Trans. 2* **2000**, 2077.
(21) Otto, W. H.; Keefe, M. H.; Splan, K. E.; Hupp, J. T.; Larive, C. K. *Inorg. Chem.* **2002**, *41*, 6172
(22) (a) Stahl, N. G.; Zuccaccia, C.; Jensen, T. R.; Marks, T. J. *J. Am. Chem. Soc.* **2003**, *125*, 5256. (b) Macchioni, A.; Romani, A.; Zuccaccia, C.; Guglielmetti, G.; Querci, C. *Organometallics* **2003**, *22*, 1526. (c) Martínez-Viviente, E.; Rüegger, H.; Pregosin, P. S.; López-Serrano, J. *Organometallics* **2002**, *21*, 5841. (d) Valentini, M.; Pregosin, P. S.; Rüegger, H. *J. Chem. Soc., Dalton Trans.* **2000**, 4507.
(23) Stejskal, E. O.; Tanner, J. E. *J. Chem. Phys.* **1965**, *42*, 288.
(24) Dymock, K.; Palenik, G. J. *Acta Crystallogr. B* **1974**, *30*, 1364.
(25) Churchill, M. R.; Churchill, D. G.; Huynh, M. Y. H.; Takeuchi, K. J.; Castellano, R. K.; Jameson, D. L. *J. Chem. Cryst.* **1996**, *26*, 179.
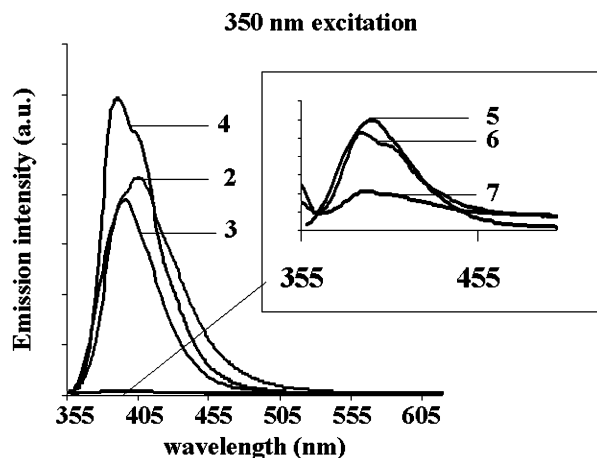
Figure 7. Normalized room-temperature emission spectra of compounds **2**−**7** in tetrachloroethane. Inset provides magnified view of spectra of rhenium complexes.

with $Re(CO)_5Br$ to yield $Re(CO)_3Br[(pz^{pyrene})_2CH_2]$ (**5**) and $Re(CO)_3Br[(pz^{pyrene})_2CH(^nPr)]$ (**6**). The solid-state structure of $Re(CO)_3Br[(pz^{pyrene})_2CH(^nPr)]$ is supramolecular, comprising two-dimensional sheets organized by $\pi-\pi$ stacking and edge-to-face CH$-\pi$ stacking interactions. NMR experiments demonstrate that isomers are present in solution that have the common feature of C−H···Br hydrogen-bonding interactions involving the acidic hydrogen on the central bis-(pyrazolyl)alkane carbon, but that differ by restricted rotation about the pyrazolyl−pyrenyl bond. Pulsed-field gradient spin−echo NMR (PGSE-NMR) experiments show that the complexes are monomeric in tetrachloroethane. The bis-[(pyrenyl)pyrazolyl]alkanes exhibit monomer-based rather than excimer-based fluorophore emissions in dilute tetrachloroethane solution when irradiated with light at any wavelength corresponding to their absorption bands. The metal complexes are essentially nonluminescent; the ligand fluorescence is quenched by an intramolecular process in this system rather than the wavelength of emission being shifted by complexation to rhenium.

Supporting Information Available: Full experimental details and characterization data for compounds **1**−**5** and **7**. ^{1}H, DQCOSY, and homonuclear *J*-resolved NMR spectra for compounds **2**−**7**. Crystallographic data for compound **7**. Full details of the molecular and supramolecular structure of **6**. Crystallographic information files (CIF) files for **6** and **7**. Details and data from the PGSE NMR experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034631G