Keywords: acetylene · aldol reactions · asymmetric synthesis · camphor · methyl ketone

[1] Reviews on the asymmetric aldol condensation: a) D. A. Evans, J. V. Nelson, T. R. Taber, *Top. Stereochem*. **1982**, *13*, 1; b) S. Masamune, W. Choy, J. S. Petersen, L. R. Sita, *Angew. Chem.* **1985**, *97*, 1; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 1; c) *Comprehensive Organic Chemistry*, *Vol. 2* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon, Oxford, **1991**; d) C. H. Heathcock in ref. [1c], p. 133; e) M. Kim. S. F. Williams, S. Masamune, in ref. [1c], p. 239; f) I. Paterson, in ref. [1c], p. 301; g) A. S. Franklin, I. Paterson, *Contemp. Org. Synth.* **1994**, *1*,317; h) M. Braun in *Stereoselective Synthesis. (Houben-Weyl)*, *Vol. E21/3* (Eds.: G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann), Thieme, Stuttgart, **1996**, p. 1603.

[2] Extensive list of chiral auxiliaries: a) A.-ur Rahman, Z. Shah, *Stereoselective Synthesis in Organic Chemistry*, Springer, Berlin, **1993**; b) J.Seyden-Penne, *Chiral Auxiliaries and Ligands in Asymmetric Synthesis*, Wiley, New York, **1995**; c) D. J. Ager, I. Prakash, D. R. Schaad, *Chem Rev.* **1996**, *96*, 835.

[3] S. Hanessian, *Total Synthesis of Natural Products: The Chiron Approach*, Pergamon, Oxford, **1983**.

[4] a) C. H. Heathcock; M. C. Pirrung, C. T. Buse, J. P. Hagen, S. D. Young, J. E. Sohn, *J. Am. Chem. Soc.* **1979**, *101*, 7077; b) C. H. Heathcock, M. C. Pirrung, J. Lampe, C. T. Buse, S. D. Young, *J. Org. Chem.* **1981**, *46*, 2290; c) N. A. Van Draanen, S. Arseniyadis, M. T. Crimmins, C. H. Heathcock, *ibid.* **1991**, *56*, 2499; d) S. Masamune, SK. A. Ali, D. L. Snitman, D. S. Garvey, *Angew. Chem.* **1980**, *92*, 573; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 557; e) S. Masamune, W. Choy, F. A. L. Kerdesky, B. Imperiali, *J. Am. Chem. Soc.* **1981**, *103*, 1566; f) C. Siegel, E. R. Thornton, *ibid.* **1989**, *111*, 5722; g) B. M. Trost, H. Urabe, *J. Org. Chem.* **1990**, *55*, 3982; h) C. H. Heathcock, C. T. White, J. J. Morrison, D. VanDerveer, *ibid.* **1981**, *46*, 1296; i) D. A. Evans, J. V. Nelson, E. Vogel, T. R. Taber, *J. Am. Chem. Soc.* **1981**, *103*, 3099; j) B. R. Lagu, H. M. Crane, D. C. Liotta, *J. Org. Chem.* **1993**, *58*, 4191; k) S. Figueras, R. Martín, P. Romea, F. Urpí, J. Vilarrasa, *Tetrahedron Lett.* **1997**, *38*, 1637.

[5] a) C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, J. Lampe, *J. Org. Chem.* **1980**, *45*, 1066; b) C. H. Heathcock, S. D. Young, J. P. Hagen, M. C. Pirrung, C. T. White, D. Vanderveer, *ibid.* **1980**, *45*, 3846.

[6] For a detailed information on this topic, see: a) M. Braun, *Angew. Chem.* **1987**, *99*, 24; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 24; b) M. Braun in *Advances in Carbanion Chemistry, Vol. 1* (Ed.: V. Snieckus), Jai, London, **1992**, p. 177.

[7] Aldol reactions of achiral methyl ketones with achiral aldehydes on use of chiral boron reagents: a) I. Paterson, J. M. Goodman, *Tetrahedron Lett.* **1989**, *30*, 997; b) P. V. Ramachandran, W. Xu, H. C. Brown, *Tetrahedron Lett.* **1996**, *37*, 4911; c) A. Bernardi, C. Gennari, J. M. Goodman, I. Paterson, *Tetrahedron Asymmetry* **1995**, *6*, 2613; on use of chiral titanium reagents: d) R. O. Duthaler, P. Herold, W. Lottenbach, K. Oertle; M. Riediker, *Angew. Chem.* **1989**, *101*, 490; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 495; on use of chiral palladium(II) reagents: e) M. Sodeoka, R. Tokunoh, F. Miyazaki, E. Hagiwara, M. Shibasaki, *Synlett* **1997**, 463; on use of external chiral catalysts: f) K. J. Hale, S. Manaviazar in *Advanced Asymmetric Synthesis*, *Vol. 2* (Ed.: G.-R. Stephenson), Chapman and Hall, London, **1996**, p. 27; g) T. Mukaiyama, *Aldrichimica Acta* **1996**, *29*, 59.

[8] Recent examples from chiral acetate imide enolates: a) K. Otsuka, T. Ishizuka, K. Kimura, T. Kunieda, *Chem. Pharm. Bull.* **1994**, *42*, 748; b) T.-H. Yan, A.-W. Hung, H.-C. Lee, C. S. Chang, W.-H. Liu, *J. Org. Chem.* **1995**, *60*, 3301; c) T. H. Yan, A.-W. Hung, H.-C. Lee, C. S. Chang, *ibid.* **1994**, *59*, 8187; from chiral *N*-acetyl sultam enolates: d) W. O. Oppolzer, C. Starkemmann, *Tetrahedron Lett.* **1992**, *33*, 2139; from Fisher carbene enolates: e) T. S. Powers, Y. Shi, K. J. Wilson, W. D. Wolff, *J. Org. Chem.* **1994**, *59*, 6882.

[9] a) C. Palomo, M. Oiarbide, A. Gonzalez, J. M. García, F. Berree, A. Linden, *Tetrahedron Lett.* **1996**, *37*, 6931; b) C. Palomo, F. Berree, A. Linden, J. M. Villalgordo, *J. Chem. Soc. Chem. Commun.* **1994**, 1961.

[10] For an earlier camphor-based ester acetate aldol approach exploiting this concept in another way, see G. Helmchen, U. Leikauf, I. Taufer-knöpfel, *Angew. Chem.* **1985**, *97*, 874; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 874.

[11] Review on camphor-based chiral auxilaries: W. Oppolzer, *Tetrahedron* **1987**, *43*, 1969.

[12] H. E. Zimmerman, M. D. Traxler, *J. Am. Chem. Soc.* **1957**, *79*, 1920.

[13] M. Kagawa, *Chem. Pharm. Bull.* **1959**, *7*, 306

[14] a) M. M. Midland, *J. Org. Chem.* **1975**, *40*, 2250; b) M. M. Midland, J. I. McLoughlin, R. T. Werley, Jr., *Org. Synth. Coll.* **1993**, *Vol 8*, p 391.

[15] The addition of lithium acetylide to (1*R*)-(+)-camphor has been previously reported to give the *endo* adduct: a) M.-L. Capmau, W. Chodkiewicz, P. Cadiot, *Bull. Soc. Chim. Fr.* **1968**, 3233. Other authors, however, suggest that the *exo* adduct was produced instead: b) C. D. Johnson, S. Lane, P. N. Edwards, P. J. Taylor, *J. Org. Chem.* **1988**, *53*, 5130; c) P. Bovonsombat, E. McNelis, *Tetrahedron Lett.* **1993**, *34*, 4277. In our hands the procedure of Midland[14] gives reproducible results. Product **5** can also be obtained by direct hydration of the crude *endo*:*exo* mixture of **4** followed by a single crystallization from hexane (yield, 90%).[20]

[16] J. M. Aizpurua, C. Palomo, A. L. Palomo, *Can. J. Chem.* **1984**, *62*, 336.

[17] Observed values **9a**: +15.5 ($c = 0.9$ in EtOH) [Published value: +17.9 ($c = 2.3$ in EtOH 95%)[10]]; **9e**: +41.7 ($c = 1.0$ in $CHCl_3$) [Published value: +40.5 ($c = 0.6$ in $CHCl_3$)[10]]; **9g**: +53.0 ($c = 1.0$ in $CHCl_3$) [Published value: +53.2 ($c = 1.0$ in $CHCl_3$)[7d]].

[18] T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, Y. Kamiya, *J. Am. Chem. Soc.* **1989**, *111*, 4392.

[19] Every attempt at attacking the carbonyl group of the corresponding aldols with both lithium and Grignard reagents led to unsatisfactory results.

[20] Crystallographic data (excluding structure factors) for the structures **5**, **7g**, and **13** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100315. Copies of the data can be obtained free of charge on application to: CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44) 1223-336033; e-mail: deposit@chemcrys.cam.ac.uk).

[{Pt(CN)($C_{10}H_{21}N_4$)}$_6$]: A Luminescent Hexanuclear Platinum(II) Macrocycle Containing Chelating Dicarbene and Bridging Cyanide Ligands**

Siu-Wai Lai, Kung-Kai Cheung, Michael Chi-Wang Chan, and Chi-Ming Che*

Transition metal mediated self-assembly reactions are a versatile strategy for generating supermolecules with appealing structural and spectroscopic properties.[1–6] In this context we are interested in luminescent molecular hosts[7] composed of square-planar platinum(II) complexes as building blocks, since such materials could have applications in host–guest photochemistry and as novel luminescent sensors. Fujita et al.[1] and Stang et al.[5a, b] reported the preparation of tetranuclear platinum(II) compounds with pyridine-based ligands. Here we describe the crystal structure of a novel luminescent hexanuclear platinum(II) macrocycle bearing cyclic dicarbene and bridging cyanide ligands.

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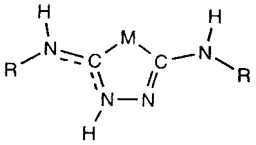

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The synthesis of a mononuclear platinum(II) complex with the chelating $C_4H_9N_4$ ligand (**1**, $R = CH_3$) by addition of methyl isocyanide and hydrazine to $K_2[PtCl_4]$ in water has long been known.[8] Subsequent investigations revealed the $[C_4H_9N_4]$ moiety to be a monoanionic planar "resonance-stabilized" dicarbene ligand.[9] In contrast, heating K_2PtCl_4, *tert*-butyl isocyanide, and hydrazine hydrate in water at reflux for one hour resulted in the formation of $[Pt(CN)(C_{10}H_{21}N_4)]_6$ (**2**), which was isolated as acetonitrile-solvated yellow crystals upon recrystallization from acetonitrile/diethyl ether.

The X-ray structure of **2** (Figure 1)[10] shows it to be a rare example of a Pt_6 macrocycle.[11] The core of **2** consists of six platinum atoms linked through crystallographically disordered[10] cyanide units and is puckered in a chairlike conformation. Alternatively, this 18-membered ring can be regarded as a open cubane-type structure in which a pair of opposite corners is missing. The other six corners are occupied by platinum atoms, and the bridging cyanide ligands form the sides. The angles within the core are in accordance with this geometry: the CN-Pt-CN angles at the corners are almost orthogonal (av 92.4°), while the Pt-C-N and Pt-N-C groups are nearly linear (av 174°).

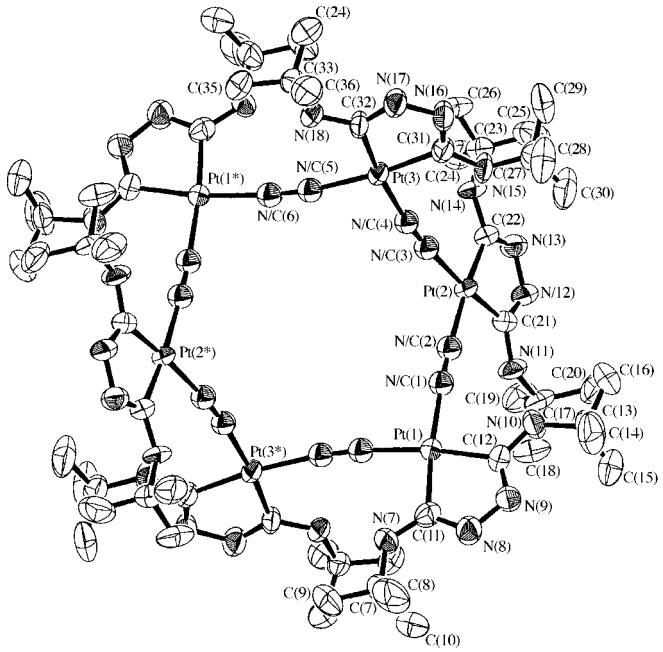

Figure 1. Crystal structure of **2** with atomic numbering scheme (40% probability ellipsoids). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt(1)–N/C(1) 2.05(1), N/C(1)–N/C(2) 1.13(2), Pt(2)–N/C(2) 2.03(1), Pt(2)–N/C(3) 2.02(1), N/C(3)–N/C(4) 1.17(1), Pt(3)–N/C(4) 2.02(1), Pt(1)–C(11) 2.00(1), Pt(1)–C(12) 2.01(1), Pt(2)–C(21) 1.97(1), Pt(2)–C(22) 1.97(1), N(12)–C(21) 1.31(2), N(12)–N(13) 1.41(1), N(13)–C(22) 1.30(2), Pt(3)–C(31) 2.01(1), Pt(3)–C(32) 1.98(1); N/C(1)-Pt(1)-N/C(6) 92.2(5), N/C(2)-Pt(2)-N/C(3) 92.5(5), N/C(4)-Pt(3)-N/C(5) 92.4(5), Pt(1)-N/C(1)-N/C(2) 174(1), Pt(2)-N/C(2)-N/C(1) 175(1), Pt(2)-N/C(3)-N/C(4) 175(1), Pt(3)-N/C(4)-N/C(3) 174(1), C(11)-Pt(1)-C(12) 78.8(6), C(21)-Pt(2)-C(22) 78.2(6), C(31)-Pt(3)-C(32) 78.7(5), Pt(2)-C(22)-N(13) 117.5(10), Pt(2)-C(22)-N(14) 121(1), N(13)-C(22)-N(14) 120(1).

The $C_{10}H_{21}N_4$ motif (see **1**, R = *t*Bu) is analogous to the $C_4H_9N_4$ group in earlier work,[8, 9] and hence a planar PtC_2N_2 five-membered metallacycle is present. The Pt–carbene distances are in the range 1.97(1)–2.01(1) Å and are similar to those in the platinum(II) complexes *trans*-[Pt{C(NEt$_2$)(O-C(O)Ph)}(PPh$_3$)I$_2$] (1.969(7) Å),[12] [Pt(H)(CH$_2$CN)-{C(NC$_3$H$_6$)N(H)(*p*-MeOC$_6$H$_4$)}(PPh$_3$)] (2.069(4) Å),[13] and *trans*-[Pt(Me){C(NMe$_2$)Me}(PMe$_2$Ph)$_2$]PF$_6$ (2.079(13) Å).[14] Intriguingly, the Pt–C(sp^3) distance of 2.147(11) Å in the latter is only slightly longer, and this can be attributed to the *trans* influence of the carbene ligand. Nevertheless, the carbene description is vindicated by the sp^2-type hybridization of the respective carbon centers in **2**; the angles at C(21) are 122.8(10), 121(1), and 115.7(9)°. Formation of **2** can be explained as follows: two coordinated *t*BuNC ligands react with hydrazine to give the chelating dicarbene ligand, and platinum(II)-mediated dealkylation of *t*BuNC gives rise to the cyanide ligands. We note that heating a solution of $[PtCl_4]^{2-}$ and *t*BuNC in water for one hour similarly generated a partially dealkylated species, namely, $[Pt(CNtBu)_2(CN)_2]$.[15]

The absorption spectrum of **2** in methanol (Figure 2a) exhibits an intense band at 356 nm. The very high extinction coefficient of $\varepsilon_{max} = 18000\ dm^3mol^{-1}cm^{-1}$ indicates a spin-allowed charge-transfer (CT) transition, and we tentatively assign this to a Pt $\rightarrow\pi^*$(carbene) transition. Transitions within the chelating dicarbene groups are discounted, since they would occur at higher energy. The alternative assignment as a Pt $\rightarrow\pi^*(CN^-)$ transition is not favored, since mononuclear Pt^{II} cyanide derivatives bearing π-acid ligands such as phosphane or alkyl isocyanide do not absorb strongly at $\lambda > 300$ nm. For example, the lowest energy bands of [Pt(dppe)(CN)$_2$] (dppe = 1,2-bis(diphenylphosphanyl)ethane) and [Pt(CN*t*Bu)$_2$(CN)$_2$] appear at 294 and 282 nm respectively in methanol.[16] Furthermore, the Pt $\rightarrow\pi^*(CN^-)$ transition of $[Pt(CN)_4]^{2-}$ occurs at 280 nm.[17] The relatively low energy of the Pt $\rightarrow\pi^*$(carbene) transition means that the carbene ligand can readily be exploited in photochemical studies of metal-to-ligand charge transfer (MLCT) in platinum(II) derivatives.

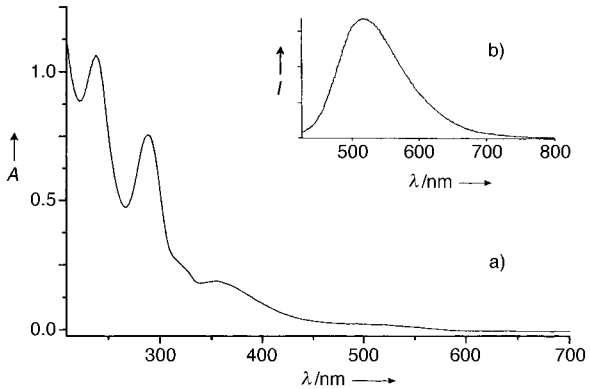

Figure 2. a) UV/Vis spectrum of **2** in methanol. b) Emission spectrum of **2** in CH_2Cl_2 (intensity *I* in arbitrary units).

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Upon excitation at 350 nm at 301 K, crystalline **2** shows a structureless emission band centered at 514 nm, which at 77 K is blue-shifted to 507 nm. In a degassed solution in CH_2Cl_2 at 301 K, an emission band is observed at 519 nm with a lifetime of 0.22 μs (Figure 2b). The emission at $\lambda > 500$ nm provides further evidence for a Pt→π*(carbene) transition, since $[Pt(CN)_4]^{2-}$ displays an intense emission band at 408 nm only with a shoulder at 460 nm.[17] Despite previous studies,[18] we believe that this is the first observation of an emissive metal→π*(carbene) CT excited state in solution at room temperature. The long lifetime and high energy (ca. 2.8 eV, E_{0-0} taken as 450 nm) of the excited state imply that these platinum(II) species can undergo bimolecular photoreactions, and preliminary results confirm that the emission of **2** is quenched by *N*,*N*′-dimethyl-4,4′-bipyridinium hexafluorophosphate in dichloromethane. Future work will be directed towards probing the excited state reactivities of carbene complexes by utilizing the MLCT emission of the platinum(II) carbene moiety.

Experimental Section

2: A solution of $K_2[PtCl_4]$ (0.20 g, 0.48 mmol), *tert*-butyl isocyanide (0.20 mL, 1.93 mmol), and hydrazine hydrate (0.10 mL, 2.06 mmol) in water was heated to reflux for 1 h. The volatile components were removed in vacuo, and the residue was extracted with acetonitrile/diethyl ether. Slow evaporation of this solution at 5 °C yielded yellow crystals (yield 32 %). ^{1}H NMR (300 MHz, $CDCl_3$, 27 °C): $\delta = 1.40$ (s, *t*Bu); IR (Nujol): $\tilde{\nu} = 3453$, 3412 (N–H); 2141 (C≡N); 1562, 1535 cm^{-1} (C=N); UV/Vis (methanol): λ_{max} (ε) = 238 (95000), 288 (68000), 316 (22000), 356 nm (18000); FAB-MS: *m/z* (%) = 2510 (100) $[Pt(CN)(C_{10}H_{21}N_4)]_6^+$, 1255 (50) $[Pt(CN)(C_{10}H_{21}N_4)]_3^+$. Satisfactory elemental analysis.

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[1] a) M. Fujita, K. Ogura, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1471–1482; b) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature* **1995**, *378*, 469–471.
[2] J. P. Sauvage, *Acc. Chem. Res.* **1990**, *23*, 319–327.
[3] J. M. Lehn, A. Rigault, *Angew. Chem.* **1988**, *100*, 1121–1122; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1095–1097.
[4] D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196.
[5] a) P. J. Stang, D. H. Cao, S. Saito, A. M. Arif, *J. Am. Chem. Soc.* **1995**, *117*, 6273–6283; b) P. J. Stang, B. Olenyuk, *Angew. Chem.* **1996**, *108*, 798–802; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 732–736; c) P. J. Stang, N. E. Persky, J. Manna, *J. Am. Chem. Soc.* **1997**, *119*, 4777–4778.
[6] C. K. Chan, K. K. Cheung, C. M. Che, *Chem. Commun.* **1996**, 227–228.
[7] a) R. V. Slone, J. T. Hupp, C. L. Stern, T. E. Albrecht-Schmitt, *Inorg. Chem.* **1996**, *35*, 4096–4097; b) B. C. Tzeng, W. C. Lo, C. M. Che, S. M. Peng, *J. Chem. Soc. Chem. Commun.* **1996**, 181–182.
[8] L. Tschugajeff, M. Skanavy-Grigorjewa, A. Posnjak, *Z. Anorg. Allg. Chem.* **1925**, *148*, 37–42.
[9] a) G. Rouschias, B. L. Shaw, *J. Chem. Soc. A* **1971**, 2097–2104; (b) W. M. Butler, J. H. Enemark, J. Parks, A. L. Balch, *Inorg. Chem.* **1973**, *12*, 451–457.
[10] Crystal data for **2**: $C_{66}H_{126}N_{30}Pt_6 \cdot 10\,CH_3CN$; M = 2920.94, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.713(6)$, $b = 18.186(6)$, $c = 14.042(8)$ Å, $\alpha = 101.03(3)$, $\beta = 105.84(4)$, $\gamma = 113.83(3)°$, $V = 3106(2)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.561$ g cm^{-3}, $\mu = 67.55$ cm^{-1}, $F(000) = 1420$, $T = 301$ K. A yellow crystal of dimensions $0.25 \times 0.20 \times 0.35$ mm^3 was used for data collection at 301 K on a Rigaku AFC7R diffractometer (graphite-monochromatized $Mo_{K\alpha}$ radiation; $\lambda = 0.71073$ Å), ω-2θ scan mode, ω-scan angle $(0.73+0.35 \tan\theta)°$, scan speed 16.0° min^{-1} (up to six scans for reflections with $I < 15\sigma(I)$). Measurement range: $2\theta_{max} = 46°$; *h*: 0 to 16; *k*: −19 to 19; *l*: −15 to 15. Three standard reflections were measured after every 300 reflections and showed a decay of 3.74 %. The intensity data were corrected for decay, Lorentz, and polarization effects, and empirical absorption corrections based on the ψ scan of six strong reflections (min./max. transmission factors 0.671/1.000) were made. Of 9041 reflections measured, 8644 were unique with $R_{int} = 0.026$. 5738 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The structure was solved by Patterson methods, expanded by Fourier methods (PATTY), and refined by full-matrix least squares with the software package TeXsan on a Silicon Graphics Indy computer. The crystallographic asymmetric unit consists of one half of the complex molecule and five molecules of acetonitrile. The six CN groups forming the 18-membered ring system were disordered; all the atomic sites were occupied half by N atoms and half by C atoms. Atoms N(1) to N(6) and C(1) to C(6) were refined isotropically with occupation numbers of 0.5, whereby the positions and thermal parameters of the C atoms were constrained to those of the corresponding N atoms (i.e. N/C(1) to N/C(6)). The C and N atoms of the five solvent molecules had large temperature factors and were also refined isotropically. The other non-hydrogen atoms of the complex were refined anisotropically. The hydrogen atoms bonded to the N atoms of the ligand molecules were not located in difference Fourier synthesis. The other 69 H atoms (including solvent) were introduced at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms and were not refined. Convergence for 490 variable parameters by least-squares refinement on *F* with $w = 4F_o^2/\sigma^2(F_o^2)$ ($\sigma^2(F_o^2) = [\sigma^2(I) + (0.035F_o^2)^2]$) for 5738 reflections with $I > 3\sigma(I)$ was reached at $R = 0.038$ and $wR = 0.056$ and GOF = 1.67. $(\Delta/\sigma)_{max.} = 0.04$ for atoms of the complex. The final difference Fourier map was featureless with maximum positive and negative peaks of 2.40 and −0.71 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100633. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code + (44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).
[11] a) J. Lorberth, W. Massa, M. E.-Essawi, L. Labib, *Angew. Chem.* **1988**, *100*, 1194–1195; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1160–1161; b) B. Longato, G. Bandoli, G. Trovó, E. Marasciulo, G. Valle, *Inorg. Chem.* **1995**, *34*, 1745–1750.
[12] J. T. Chen, W. H. Tzeng, F. Y. Tsai, M. C. Cheng, Y. Wang, *Organometallics* **1991**, *10*, 3954–3955.
[13] R. A. Michelin, R. Bertani, M. Mozzon, L. Zanotto, F. Benetollo, G. Bombieri, *Organometallics* **1990**, *9*, 1449–1459.
[14] R. F. Stepaniak, N. C. Payne, *Inorg. Chem.* **1974**, *13*, 797–801.
[15] L. Malatesta, F. Bonati, *Isocyanide Complexes of Metals*, Wiley, London, **1969**, p. 169.
[16] S. W. Lai, C. M. Che, unpublished results.
[17] J. W. Schindler, R. C. Fukuda, A. W. Adamson, *J. Am. Chem. Soc.* **1982**, *104*, 3596–3600.
[18] a) H. C. Foley, L. M. Strubinger, T. S. Targos, G. L. Geoffroy, *J. Am. Chem. Soc.* **1983**, *105*, 3064–3073; b) A. D. Rooney, J. J. McGarvey, K. C. Gordon, R.-A. McNicholl, U. Schubert, W. Hepp, *Organometallics* **1993**, *12*, 1277–1282; c) L. S. Hegedus, *Tetrahedron* **1997**, *53*, 4105–4128.

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