stage prior to the formation of **5**. Compound **5** was obtained by the thermal decarbonylation and condensation of 2 mol of **1**. $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ was prepared in good yield by the photoinduced decarbonylation and condensation of 2 mol of $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$.[16] Interestingly, $Os_6(CO)_{17}(\mu_4\text{-}S)_2$ can be decarbonylated to form the more highly condensed species $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$.[14] We found no evidence for this reaction with **5**. Instead, when compound **5** was heated, the cluster broke down and compound **3** was formed.

The greatest differences in structural chemistry between the disulfidoruthenium and the disulfidoosmium carbonyl cluster series lie in compounds **3** and **4**. $Os_4(CO)_{11}(\mu_4\text{-}S)_2$ has not yet been prepared. $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ is known, but it has a butterfly tetrahedral cluster of metal atoms.[17] Our efforts to decarbonylate $Os_4(CO)_{12}(\mu_3\text{-}S)_2$ to form $Os_4(CO)_{11}(\mu_4\text{-}S)_2$ have not been successful.[18] Interestingly, we have been able to transform the butterfly clusters $Os_4(CO)_{12}(\mu_3\text{-}S)(\mu_3\text{-}HC_2R)$ (R = Ph, CO_2Me) into the square clusters $Os_4(CO)_{11}(\mu_4\text{-}S)(\mu_4\text{-}HC_2R)$.[19] To date, there are no known examples of disulfidopentaosmium carbonyl clusters with which to compare to **4**.

Another difference between the two series lies in their reactivities toward CO. The ruthenium clusters are readily degraded under 1 atm of CO to give either **3** as a precipitate or **2**. The osmium compounds are much more resistant to degradation by CO. For example, $Os_6(CO)_{16}(\mu_4\text{-}S)(\mu_3\text{-}S)$ does not react significantly when treated with CO at 165 atm/210 °C for 2 days. This difference in reactivity can probably be attributed to the greater strength of the Os–Os vs. the Ru–Ru bonds.[20] Most CO addition reactions induce metal–metal bond cleavages.

Acknowledgment. The research was supported by the National Science Foundation under Grant No. CHE-8612862.

Registry No. **1**, 105121-22-0; **2**, 72282-38-3; **3**, 105121-25-3; **4**, 109433-55-8; **5**, 109433-54-7; **6**, 109466-69-5; $Ru_3(CO)_{12}$, 15243-33-1; $Ru(CO)_5$, 16406-48-7.

Supplementary Material Available: For compounds **4**–**6**, tables of complete bond angles and of anisotropic thermal parameters (*U* values) (15 pages); listings of structure factor amplitudes (54 pages). Ordering information is given on any current masthead page.

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Cyclometalated Complexes of Platinum(II): Homoleptic Compounds with Aromatic C,N Ligands

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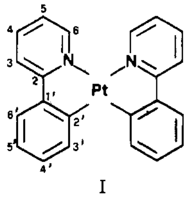
The synthesis of the five new homoleptic bis(cyclometalated) Pt(II) complexes *cis*-Pt(Phpz)$_2$ (II, $C_{18}H_{14}N_4Pt$), *cis*-Pt(Thpy)$_2$ (III, $C_{18}H_{12}N_2S_2Pt$), Pt(3-Thpy)$_2$ (IV, $C_{18}H_{12}N_2S_2Pt$), *cis*-Pt(Thpy-SiMe$_3$)$_2$ (V, $C_{24}H_{28}N_2S_2Si_2Pt$), and *cis*-Pt(Thpz)$_2$ (VI, $C_{14}H_{10}N_4S_2Pt$) from *trans*-$PtCl_2(SEt_2)_2$ and the lithiated ligands at low temperature (−78 °C) is described. All compounds are air-stable, soluble in many organic solvents, and photoreactive in solution under irradition with visible light. The strong low-energy bands in the electronic spectra in the range from 400 to 450 nm are assigned to metal to ligand charge-transfer (MLCT) transitions from a Pt(5d) orbital to an empty π^* orbital of the ligands. Most spectra show a weak absorption superimposed on the low-energy side of the strong MLCT band. This weak absorption is attributed to a singlet–triplet transition of the same type as the strong band. The complexes can be reduced electrochemically in reversible one-electron steps. Oxidation occurs also, but in a completely irreversible manner.

Introduction

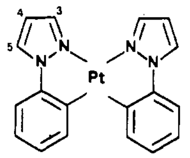
Cyclometalated complexes represent a link between classic, Werner-type coordination compounds and organometallic species.[1] We are exploring presently the possibility of synthesizing *homoleptic* complexes with C,N aromatic cycles of several transition metals.[2] Such species are promising candidates for interesting photochemical and photophysical properties.[3] The first example of a homoleptic bis complex with aromatic ligands of a d^8 metal was described recently.[4] In the present paper, we describe further examples in the series. The platinum(II) complexes I–VI are characterized by using several analytical methods.

All these compounds are air stable and they can be crystallized from several solvents. In some cases precautions, during the handling of solutions, against photoreactions have to be taken.

The synthesis, X-ray crystal structure, and several properties of I have already been published; some results have not yet been given, however. In this report I is included for the sake of completeness.



I



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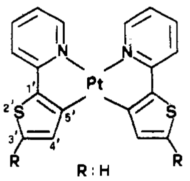
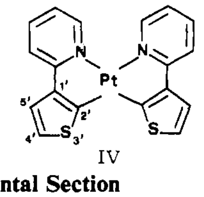


R : H

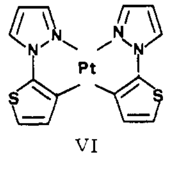
III

R : Si(CH$_3$)$_3$

V



IV



VI

Experimental Section

Measurements. Electronic spectra were recorded with a Perkin-Elmer 555 spectrophotometer. ^1H NMR spectra were collected with Varian T-60, Varian XL-300, and Bruker M-360 spectrometers. ^{13}C NMR spectra were obtained on Varian XL-300 and Bruker M-360 spectrometers at 75.5 and 90.6 MHz. Natural-abundance ^{195}Pt NMR spectra were obtained on a Bruker M-360 spectrometer with a wide-bore (20-mm) probe at 70.07 MHz (external reference $Pt(CN)_6^{2-}$ in H_2O). Mass

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Table I. Position and Extinction Coefficients of Absorption Bands ($\lambda > 350$ nm)

complex[a]	λ/nm (ϵ/mol^{-1} cm^2)
$Pt(Phpy)_2$	484 (90),[b] 402 (10 450), 376 (5430)[b]
$Pt(Phpz)_2$	424 (70)
$Pt(2\text{-}Thpy)_2$	570 (90), 550 (90),[b] 526 (130),[b] 460 (1900),[b] 420 (10 700),[b] 392 (4970), 350 (14 140)[b]
$Pt(3\text{-}Thpy)_2$	*c*, 460 (3320),[b] 420 (8500), 396 (4390)[b]
$Pt(Thpy\text{-}SiMe_3)_2$	578 (110), 536 (160),[b] 464 (3200),[b] 424 (11 700), 400 (3040),[b] 359 (18 000)
$Pt(Thpz)_2$	512 (30), 476 (96),[b] 408 (1890),[b] 364 (11 570)
$Pt(bpy)_2(PF_6)_2$[d]	370 (2750)[b]

[a] Solvent = CH_2Cl_2. [b] Shoulder. [c] Insufficient solubility for weak absorptions. [d] Solvent = H_2O.

Table II. Cyclic Voltammetry Results in Acetonitrile Solution, with 0.1 M TEAP or $(TEA)PF_6$

	potential/V vs. SCE[a]			
complex	E_{p^a}	E_{p^c}	$E_{1/2}$	E_p
$Pt(Phpy)_2$	0.26	*b*	−2.19	0.07
$Pt(Phpz)_2$	0.45	*b*	−2.67	0.08
$Pt(2\text{-}Thpy)_2$	0.33	*b*	−2.11	0.06
$Pt(Thpy\text{-}SiMe_3)_2$	0.28	*b*	−2.09	0.07
$Pt(Thpz)_2$	0.29	0.15	*c*	
$Pt(bpy)_2(PF_6)_2$[d]	*c*	*c*	−0.97 (E_{p^c}) irr	
			−1.51	(0.07)
			−2.53	(0.06)

[a] Calibrated with $Ru(bpy)_3(PF_6)_2$ in the same solvent. [b] The cathodic peak is not present. [c] Reduction or oxidation, respectively, is not observed. [d] Solvent DMF.

spectra (MS) were determined by a VG Instrument 7070E mass spectrometer. Electrochemical measurements were carried out with a Metrohm Polarecord 506 coupled with a VA Scanner E612. UV/vis and voltammetry data are given in Tables I and II. ^{1}H, ^{13}C, and ^{195}Pt NMR data are presented in Tables III–VII.

Solvents and Techniques. Solvents were dried prior to use by standard techniques. Reactions involving lithium reagents were carried out under argon atmosphere by standard syringe–septum techniques. Flash chromatography was performed by the method of Still.[5]

Reagents. 2-(2-Bromophenyl)pyridine was prepared by a typical Gomberg–Hey reaction[6] and purified by flash chromatography (hexane/acetone, 8/2). 1-(2-Bromophenyl)pyrazole was prepared according to Marxer and Siegrist.[7] 2-(2-Thienyl)pyridine and 2-(3-thienyl)pyridine were purchased from Aldrich. The latter was distilled under reduced pressure prior to use. 1-(2-Thienyl)pyrazole was synthesized by a published procedure,[8] and 2-(3-(trimethylsilyl)-2-thienyl)pyridine was synthesized by addition of trimethylsilylchloride to the lithium derivative of 2-(2-thienyl)pyridine.[9] *cis*- and *trans*-$[Pt(SEt_2)_2Cl_2]$ were prepared according to Kaufmann et al.[10]

***cis*-Bis(2-phenylpyridinato-*N*,*C*$^{2'}$)platinum(II), $Pt(Phpy)_2$ (I).** The synthesis from *trans*-$Pt(SEt)_2Cl_2$ was reported elsewhere.[4] Even if *cis*-$[Pt(SEt_2)_2Cl_2]$ was used as the starting compound, only the cis isomer was formed.

***cis*-Bis(1-phenylpyrazolato-*N*,*C*$^{2'}$)platinum(II), $Pt(Phpz)_2$ (II).** (a) A solution of *trans*-$PtCl_2(Et_2S)_2$ (1.2 g, 2.7 mmol) in 50 mL of ether/THF (4/1) was added dropwise to a stirred solution of LiPhpz (from 1.74 g (7.8 mmol) of 1-(2-bromophenyl)pyrazole and BuLi (7.2 mL, 1.5 equiv)) in ether at −78 °C. The solution was stirred for 2 h at this temperature and further for 20 min at room temperature.

The reaction mixture was hydrolyzed with water. The aqueous phase was extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$), and the volume was reduced to 50 mL. Cooling to −15 °C yielded 0.06 g of the yellow complex. After flash chromatography (hexane/acetone, 3.5/1.5) of the mother liquor, 0.27 g of the complex was obtained (yield 25%). MS: *m/z* (rel intensity) 484 (30), 483 (20), 482 (20), 482 (80), 481 (M^+ = 100), 480 (80), 479 (15).

Anal. Calcd for $PtC_{18}H_{14}N_4$: C, 44.91; H, 2.94; N, 11.64. Found: C, 44.74; H, 2.93; N, 11.55.

(b) A solution of *trans*-$PtCl_2(SEt_2)_2$ (1.5 mmol, 0.67 g) in THF (10 mL) was added to a solution of the magnesium salt of 1-phenylpyrazole (4.3 mmol)[7] at 20 °C. The reaction mixture was heated to 60 °C and stirred at this temperature for 2 h. After the purification procedure described above, 0.1 g of $Pt(Phpz)_2$ was obtained (yield 13%).

***cis*-Bis[2-(2-thienyl)pyridinato-*N*,*C*$^{5'}$]platinum(II), $Pt(2\text{-}Thpy)_2$ (III).** A solution of *trans*-$PtCl_2(Et_2S)_2$ (1.4 g, 3.1 mmol) in diethylether (48 mL) and THF (12 mL) was added dropwise to a stirred solution of (4-(2-(2-thienyl)pyridinyl))lithium[9] (2.41 g, 15 mmol) in ether at −78 °C. After the solution was stirred for 30 min at −78 °C, the temperature was allowed to rise slowly to 0 °C. The reaction mixture was hydrolyzed (H_2O) at 0 °C. The organic phase was washed with NaCl solution and the aqueous phase extracted with CH_2Cl_2. The combined extracts were dried ($MgSO_4$). Upon reduction of the volume, a red solid precipitated, and after the solid was filtered and washed with cold ether, 0.76 g of pure $Pt(Thpy)_2$ was obtained. Flash chromatography (CH_2Cl_2/hexane, 3/2) of the mother liquor yielded another crop (0.14 g) of the red complex. The product can be recrystallized from dichloromethane/hexane (yield 56%). MS: *m/z* (rel intensity) 518 (30), 517 (30), 516 (85), 515 (M^+ = 100), 514 (5).

Anal. Calcd for $PtC_{18}H_{12}N_2S_2$: C, 41.93; H, 2.35; N, 5.40. Found: C, 41.9; H, 2.48; N, 5.61.

Bis[2-(3-thienyl)pyridinato-*N*,*C*$^{2'}$]platinum(II), $Pt(3\text{-}Thpy)_2$ (IV). A solution of *trans*-$PtCl_2(Et_2S)_i$ (0.35, 0.8 mmol) was added slowly to a solution of Li(3-Thpy) (from 0.5 g (3.1 mmol) of (3-thienyl)pyridine and BuLi (1.9 mL, 1 equiv) in ether (20 mL) at −78 °C). The mixture was stirred at this temperature for a further 30 min, then immersed in an ice bath and stirred at 0 °C over 30 min.

The reaction mixture was treated with ethanol at 0 °C. The solution was evaporated, and the residue was treated with 500 mL of CH_2Cl_2. After filtration and addition of hexane an orange powder was obtained. The solubility of the compound is very low in all usual solvents. MS: *m/z* (rel intensity) 518 (3), 517 (15), 516 (80), 515 (M^+ = 100), 514 (80), 513 (15).

Anal. Calcd for $PtC_{18}H_{12}N_2S_2$: C, 41.93; H, 2.35; N, 5.44. Found: C, 41.81; H, 2.28; N, 5.4.

***cis*-Bis[2-(3-(trimethylsilyl)-2-thienyl)pyridinato-*N*,*C*$^{5'}$]platinum(II), $Pt(Thpy\text{-}SiMe_3)_2$ (V).** A solution of *trans*-$PtCl_2(Et_2S)_2$ (1.6 g, 1.3 mmol) in 20 mL of ether/THF (4/1) was added dropwise to a stirred solution of Li($Thpy\text{-}SiMe_3$) (from 1.75 g (7.5 mmol) of 2-(3-(trimethylsilyl)2-thienyl)pyridine and BuLi (4 mL, 0.85 equiv)) in ether (25 mL) at −100 °C. The solution was transferred without hydrolysis on a chromatography column. The same volume of hexane was added before elution (ether/hexane, 1/1). Upon reduction of the volume, the eluate yielded a red precipitate. After filtration 0.45 g of pure $Pt(Thpy\text{-}SiMe_3)_2$ was obtained (yield 50%). MS: *m/z* rel intensity): 664 (5), 663 (10), 662 (35), 661 (45), 660 (100), 659 (M^+ = 100), 658 (70).

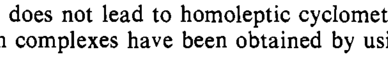
Anal. Calcd for $PtC_{24}H_{28}N_2S_2Si_2$: C, 43.71; H, 4.29; N, 4.25. Found: C, 43.65; H, 4.20; N, 4.31.

***cis*-Bis[1-(2-thienyl)pyrazolato-*N*,*C*$^{5'}$]platinum(II), $Pt(Thpz)_2$ (VI).** A solution of *trans*-$PtCl_2(Et_2S)_2$ (0.54 g, 1.2 mmol) in diethylether (16 mL) and THF (4 mL) was added dropwise to a stirred solution of (5-(1-2-thienyl)pyrazolyl))lithium[8] (1.2 g, 1.2 mmol) in ether at −78 °C. The solution was stirred for 60 min at −78 °C. The reaction mixture was hydrolyzed with 10% HCl in MeOH and was poured into a saturated solution of NaCl in H_2O. This mixture was extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$. Upon reduction of volume, a yellow-brown solid precipitated, and after filtration 0.1 g of $Pt(Thpz)_2$ was obtained (yield 17%). MS: *m/z* (rel intensity): 497 (19), 496 (35), 495 (39), 494 (100), 493 (M^+ = 100), 492 (100).

Anal. Calcd for $PtC_{14}H_{10}N_4S_2$: C, 34.07; H, 2.05; N, 11.35. Found: C, 34.33; H, 2.16; N, 11.53.

Results and Discussion

Synthesis and Mechanism. Metallocycles containing one carbon and one non-carbon ligand atom can often be synthesized by cyclometalation, i.e. formation of a chelate by spontaneous deprotonation of a carbon ligand.[11]



This method does not lead to homoleptic cyclometalated complexes. Such complexes have been obtained by using lithiated ligands.

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Table III. 360-MHz ^{1}H NMR Data[a]

ligand complex	chem shift/δ									
	H–C(3)	H–C(4)	H–C(5)	H–C(6)	H–C(2′)	H–C(3′)	H–C(4′)	H–C(5′)	H–C(6′)	SiMe$_3$
H-Phpy	7.71	7.74	7.21	8.69	7.98	7.49	———	7.44	7.98	
Pt(Phpy)$_2$[b]	7.95–7.8		7.34	8.79 (18)		8.08 (54.3)	7.25	7.14	7.66	
H-Phpz	7.67	6.33	7.79		7.62	7.31	7.15	7.31	7.62	
Pt(Phpz)$_2$	7.9	6.65	8.09			8.12 (54.3)	7.17 ——	7.14	7.31–7.27	
H-(2-Thpy)	7.73 ——	7.62	7.14	8.56	7.39	7.11	7.58			
Pt(2-Thpy)$_2$	7.5–7.3	7.75	7.11	8.61 (19)		7.5–7.3	7.69 (21.1)			
H-(3-Thpy)	7.44	7.53	7.03	8.56	7.85		7.3	7.62		
Pt(3-Thpy)$_2$[c]	7.88	8.07	7.45–7.39	8.96 (19.3)			7.56	7.45–7.39		
H-Thpy-SiMe$_3$	7.59 ——	7.54	7.05		8.53		7.21	7.57		0.34
Pt(Thpy-SiMe$_3$)$_2$	7.49	7.73	7.11	8.63 (18)			7.85 (19)			0.38
H-(2-Thpz)	7.66	6.42	7.79			7.02	6.93	7.02		
Pt(Thpz)$_2$	7.81	6.5		7.75		7.12 (21.1)	7.45 (23.2)			

[a] Internal standard Me$_4$Si. Solvent CDCl$_3$ (except where noted). Values in parentheses indicate ^3J(Pt-H) coupling constants in Hz. [b] Solvent CD$_2$Cl$_2$. [c] Solvent DMSO-d_6.

Table IV. ^{1}H NMR Chemical Shifts of Several Related Compounds[a]

complex/solvent	chem shift/δ				ref
	H-C(4)	H-C(6)	H-C(3′)	H-C(4′)	
Pt(bpy)MeCl/CD$_2$Cl$_2$	8.04	9.5, 9.13			17
Pt(bpy)MeBr/CD$_2$Cl$_2$	8.1	9.71, 9.09			18
Pt(bpy)Me$_2$/CD$_2$Cl$_2$	8.02	9.16			18
bpy/CDCl$_3$	7.77	8.67			
Pt(bpy)Me$_2$(CH$_2$Cl)Cl/CDCl$_3$		9.36			18
Pt(2-Thpy)$_2$(CH$_3$)Br/CDCl$_3$	7.9	9.72	−7.5	−7.55	13
Pt(2-Thpy)$_2$(CHCl$_2$)Cl/CDCl$_3$	−7.63	9.53	7.59	−7.63	13
Pt(Phpy)$_2$(CHCl$_2$)Cl/DMF-d_7	8.41	9.66	7.82	−7.42	13

[a] Internal standard Me$_4$Si.

Table V. ^{13}C NMR Chemical Shifts of the Protonated Ligands and the Bis(ligand)platinum(II) Complexes Measured in CDCl$_3$ with Me$_4$Si as Internal Standard

ligand complex	chem shift/δ										
	C(2)	C(3)	C(4)	C(5)	C(6)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)
H-Phpy	157.4	120.5	136.7	122.0	149.6	139.3	126.8	128.7	128.9	128.7	126.8
Pt(Phpy)$_2$	166.4	119.3	137.8	122.0	147.7	146.5	148.5	137.5	130.0	123.3	123.4
H-Phpz[a]		141.1	107.6	126.8		140.5	119.4	129.5	126.5	129.5	119.4
Pt(Phpz)$_2$		139.3	107.7	126.0		146.0	131.3	136.9	126.1	123.8	111.7
H-2-Thpy	152.5	124.4	136.5	121.8	149.4	144.8		127.5	128.0	118.6	
Pt(2-Thpy)$_2$	161.8	117.9	138.6	119.6	147.6	142.5		127.9	135.5	147.2	
H-Thpy-SiMe$_3$	152.7	125.8	136.7	121.9	149.6	143.1		149.8	134.9	119.0	
Pt(Thpy-SiMe$_3$)$_2$	161.2	118.2	138.4	119.6	147.6	143.6		147.6	141.6	148.0	
H-Thpz		141.0	107.6	128.0		142.0		120.1	126.0	114.0	
Pt(Thpz)$_2$		138.8	107.0	125.8		139.3		118.0	133.4	126.1	

[a] Reference 20.

Table VI. ^{13}C NMR Coupling Constants

complex	coupling const/Hz						
	C(2)	C(3)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)
Pt(Phpy)$_2$	76	10	1174	104.2	41.9		41
Pt(Phpz)$_2$		36.7	1144	79.5	74.4		28.5
Pt(2-Thpy)$_2$	55.9	16.1		70.3	158.8	1176	
Pt(Thpy-SiMe$_3$)$_2$	56.1				162	1161	
Pt(Thpz)$_2$		36.3		97.1	134.3	*a*	

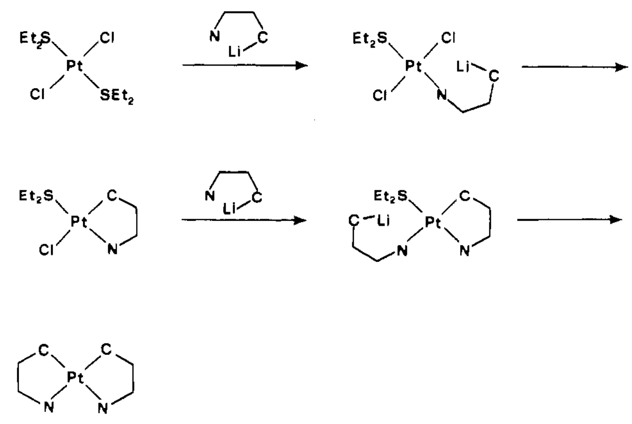
[a] Not observed.

Table VII. ^{195}Pt NMR Chemical Shifts in CHCl$_3$ as Solvent Shifts

complex	displacement/ppm[b]	complex	displacement/ppm[b]
Pt(Phpy)$_2$	721	Pt(Thpy-SiMe$_3$)$_2$	712.3
Pt(Phpz)$_2$	729.3	Pt(Thpz)$_2$	639.4
Pt(2-Thpy)$_2$	715.4	Pt(bpy)$_2$(PF$_6$)$_2$[a]	1536.5

[a] Solvent = DMF. [b] From external Na$_2$Pt(CN)$_6$.

Scheme I



The first homoleptic complexes containing only aromatic metallocycles have been obtained by similar methods.[4] In the present paper the extension of this method to new ligands is reported. The complexes are prepared at low temperature (ca. −78 °C) by addition of either *trans*- or *cis*-Pt(SEt$_2$)$_2$Cl$_2$ to a solution of the lithiated ligand. After hydrolysis and purification only one cyclometalated product (vide infra) is obtained. Scheme I represents a possible reaction pathway.

The fact that we have never found evidence for the mono chelate compound, might lead to the conjecture that the two chelate rings

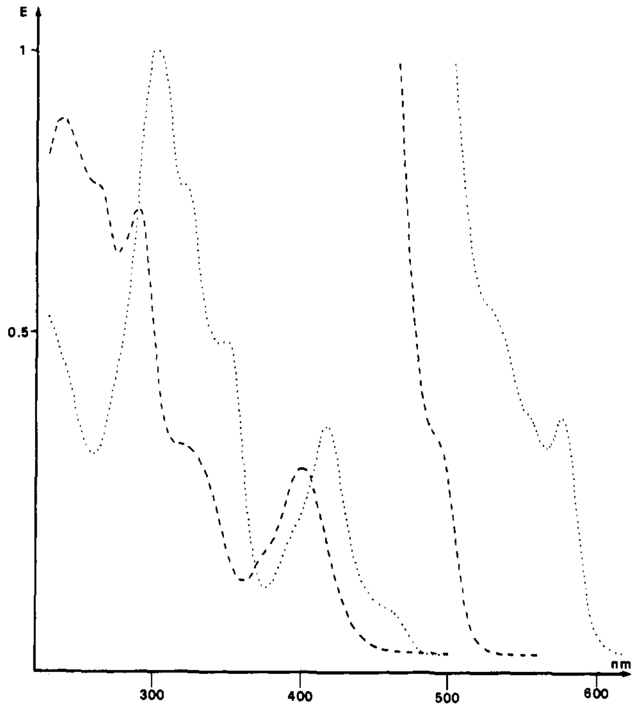


Figure 1. UV/vis spectra of Pt(Phpy)$_2$ (- -) and Pt(Thpy)$_2$ (···) in CH_2Cl_2 at 298 K.

are not formed in independent steps, and the mechanism could include the interaction of the platinum substrate with oligomers of the lithiated ligand. More recent work on mixed-ligand complexes,[12] however, shows that this is not the case, and we must assume therefore a more rapid reaction for the coordination of the second ligand as compared to the first one.

Reactivity. All compounds described in the present article are photoreactive in several solvents. Detailed investigations of these reactions show that in cases like CH_2Cl_2 and $CHCl_3$ a sterospecific *photochemical oxidative addition* (POA) occurs.[13] It takes place by irradiation with visible light, and the compounds have to be handled therefore with the necessary precautions. Alkyl iodides react even in the absence of light in a similar way.

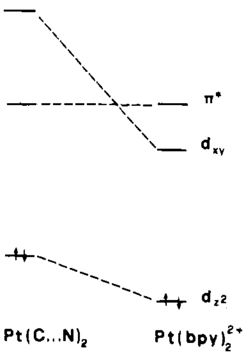
UV/Vis Spectra. Figure 1 shows the UV/vis spectra of Pt(2-Thpy)$_2$ and Pt(Phpy)$_2$. They represent typical cases for this series. Further data on all compounds are given in Table I. For comparison, the data for Pt(bpy)$_2^{2+}$ are also given.

All cyclometalated complexes have absorption bands in the visible region as opposed to Pt(bpy)$_2^{2+}$. All complexes except Pt(Thpz)$_2$ have one band between 400 and 440 nm with $\epsilon \approx 10^4$ M^{-1}/cm^{-1}. Since two C···N ligands almost certainly cause d–d splittings larger than those for two bpy ligands, no d → d transitions are expected in this spectral region. The complex Pt(en)(CN)$_2$, which is similar to the present series as far as ligand atoms are concerned, has its d → d transitions below 230 nm.[14]

The observed transitions are therefore most probably metal to ligand charge-transfer (MLCT) or ligand-centered (LC) bands. The general analogies with the MLCT-absorption bands in Ru(II)–polypyridine complexes and more detailed investigations in crystalline Pt(phpy)$_2$[15] led us to the assignment of MLCT to these transitions. The long-wavelength shoulders can then be explained as transitions to the corresponding triplet states, whose intensity is relatively large due to the strong spin–orbit coupling of Pt(II).

Cyclic Voltammetry. Table II gives the results of the cyclic voltammetry measurements of the cyclometalated complexes. There is one more or less reversible reduction wave at ca. −2.1 to −2.7 V (vs. SCE, see Table II).

Scheme II



The cyclometalated complexes are thus less easily reducible than Pt(bpy)$_2^{2+}$, which shows two reversible one-electron waves at −1.51 and −2.53 V, respectively, and in addition one irreversible wave at −0.97 V. The latter can be attributed to a metal-centered Pt(II) → Pt(I) reduction. Its absence in the cyclometalated complexes points to a different character of the LUMO in Pt(C···N)$_2$ and Pt(bpy)$_2^{2+}$, respectively. The former have their ligand π^* orbitals lowest, whereas it is the $d\sigma^*$ ($d\sigma^* = d_{xy}$) level in the latter, in agreement with the positions of C and N in the spectrochemical series. Moreover the reduction potentials follow the energy of the first $\pi \rightarrow \pi^*$ transition of the ligands. The reduction is therefore tentatively assigned to a ligand-centered process. This explanation corroborates with the interpretation of the UV/vis spectra. The completely irreversible anodic wave at E_p varying from +0.26 to +0.45 V must be due to a Pt(II) → Pt(III) oxidation, followed by a very fast chemical process, probably a reaction with the solvent. Within the accessible potential range, no oxidation can be observed for Pt(bpy)$_2^{2+}$. This means that, in agreement with the model used before, the strong σ-donor C···N destabilizes the HOMO ($d\sigma^* = d_{z^2}$) stronger in Pt(C···N)$_2$ compared to Pt(bpy)$_2^{2+}$. The orbital energies therefore correlate between Pt(C···N)$_2$ and Pt(bpy)$_2^{2+}$ as shown in Scheme II.

^{1}H NMR. Proton NMR data for the "free" ligands (C–H) and complexes are compiled in Table III. The assignments of the resonances are made by spin multiplicities, coupling constants, and in some case homonuclear decoupling experiments or through the measurement of the nuclear Overhauser effect. Coupling constants of ^{195}Pt ($I = ^1/_2$, 34% natural abundance) with ^{1}H are approximate ($\simeq$1 Hz), due to the broadness of the satellites.

The metalation of the ligand is clearly indicated by the integral value and the coupling constant $^3J(^{195}Pt-^1H)$.

Chemical Shifts. The downfield shift ($\simeq$0.2 ppm) of the β-proton Pt–N–C–H is weak compared to those of the bipyridine compounds ($\simeq$0.7 ppm; Table IV) (the trans influence of an alkyl is similar to that of an aryl ligand[16]). The comparison with the shifts of these protons in the Pt(IV)[13] complexes (Table IV), the oxidized species, clearly indicate π-back-bonding in the Pt(II) complexes.

The shifts of the phenyl protons H–C(4′) and H–C(5′) and the ring protons of the heterocycles (other than Pt–N–C–H) are due to the π-bonding,[19] as judged by comparison of the values for Pt(II) and Pt(IV) complexes. The strong shift of H–C(6′) in the phenyl ring, on the other hand, is due to the rigid conformation of the ligand in the complex.

^{13}C NMR. The ^{13}C NMR data of ligands and complexes are compiled in Tables V and VI. The assignments are made by comparison of ordinary (nondecoupled) and SFORD (single-frequency off-resonance decoupled) spectra in relation to the proton attributions. For some cases comparison between the

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complexes is necessary. The weak resonances are assigned to quaternary carbon atoms, which experience no nuclear Overhauser enhancement. The bridging carbons are found by comparison of the pyridine with the pyrazole derivatives; the carbon directly bound to platinum is found by comparison of the free ligand shifts with those of the coordinated ligand and also by the $^1J(^{195}Pt-^{13}C)$ coupling constant.

The coupling constants $^nJ(^{197}Pt-^{13}C)$ are measured from BB (broad band) decoupled spectra or sometimes from SFORD spectra.

Chemical Shifts. The upfield shift shown by C(6)py and C(3)pz can be explained by σ'_d (contribution due to electron circulation in remote orbitals[21]). The diminution of the paramagnetic contribution of the nitrogen lone pair, when it is used in the σ-bond between platinum and pyridine, will also contribute to the shielding of these carbon atoms.

Two terms in the expression of the paramagnetic screening factor σ_p derived by Pople can explain the downfield shift of the carbon atom directly bonded to the platinum:[22] ΔE, a mean value of all relevant electronic excitation energies, and Q_{AB}, a complex term involving the anisotropy of the p orbitals, which is proportional to the π-bond order of aromatic systems.[23] The sign of the shift can thus be understood, whereas the large number of contributing factors makes a quantitative correlation not feasible.

Coupling Constants. The ^1J coupling constants of our organometallic compounds are near the upper limit of the coupling constants measured for Pt–C(sp^2) bonds. Pidcock et al. report a constant of 1.186 Hz for Pt(COD)(2-thienyl)$_2$ and constants ranging from 1.080 to 1.110 Hz for a series of Pt(COD)(C_6H_4X)$_2$ compounds (X = Me, Cl, MeO, H).[24] These authors explain the high value of these constants by the position occupied by COD in the trans-influence series. In our case, we have an aromatic nitrogen compound which has a stronger trans influence than that of the COD, and a constant of 754 Hz has been measured for Pt(C_6H_5)(py)XY.[25]

The coupling constants follow the series alkyl < aryl and carbene < carbonyl. It seems unlikely that the differences between the constants of our complexes and those of Pt–phenyl compounds (505–858 Hz)[25] are due to a different hybridization.

The triplet excitation energy[26] is smaller for the cyclometalated compounds than for the complexes already described, and we have the feeling that the large value of the coupling constant is related to the small excitation energy.

The $^2J(^{195}Pt-^{13}C)$ coupling constants are observed for the phenyl or the thienyl group only for the carbon atoms that do not form a bridge between the two rings in one ligand. For the pyridine, we have observed the coupling of the C(2) atom. No coupling is observed for C(6).

The values of 30 and 32 Hz for C(2) and C(6), respectively, of Pt(bpy)(en)$^{2+}$,[27] which are considerbly smaller for C(2) but larger for C(6), as compared to the values for our complexes (Table VI), indicate a smaller Pt–N interaction in Pt(Phpy)$_2$ as compared with the Pt–N interaction in the Pt(bpy) moiety and a direct coupling through the Pt–C bond enhancing $^3J(^{195}Pt-^{13}C)$. The $^2J(^{195}Pt-^{13}C)$ coupling constants are bigger than the $^3J(^{195}Pt-^{13}C)$ coupling constants contrary to the behavior of Pt(phenyl) compounds. Contrary to the work of Clark and Ward,[25] no correlation has been found between the constants of different order.

^{195}Pt NMR. The values of the ^{195}Pt chemical shifts given in Table VII cover only a small part of the chemical shift range of platinum compounds, which spread over 13 000 ppm.[28] Their differences are insignificant over such a range.

The difference between the chemical shifts of the Pt(bpy)$_2$$^{2+}$ and the Pt(N⋯C)$_2$ compounds is not due to the asymmetry of the electron distribution within the 5d and 6p orbitals, because increased covalent bonding enhances charge delocalization away from the metal and induces a downfield shift.[29] However, the MLCT excitation energies of our complexes are smaller than those of the bpy compound, and the mixing of dπ orbitals with π^* orbitals give the character of a d–d transition.[30] The metallic character of a π^* orbital is in agreement with the back-bonding hypothesis developed in the ^{1}H NMR section.

Structure and Isomerism. The reaction of the lithiated ligands with the Pt(II) compound, gives potentially two isomers: the cis product with symmetry C_{2v} and the trans product with symmetry D_{2h}.

Experimentally only one product has been identified, (thin-layer chromatography) during the coarse of the reactions, and finally only this product has been isolated. The structure of Pt(Phpy)$_2$ indicates without ambiguity a cis form for this complex.[4] Comparison of Pt(Phpy)$_2$ NMR data, especially $^1J(^{195}Pt-^{13}C)$ and ^{195}Pt chemical shift, with the data of the other compounds gives clear structural information.

The ^1J coupling constant is directly dependent on the ligand in the trans position (vide supra). The measured difference for the coupling constant when the atom in trans position is N or C is approximately 300 Hz.[25] So the difference of the measured coupling constants for our complexes is too small to be caused by a difference in structure, and the magnitude of the values is proof in itself of the cis form.

The platinum chemical shifts are dependent on geometry, and the chemical shifts for the cis and trans complexes differ by several hundred ppm.[28] The differences of the measured resonances exclude a different geometry.

The cis configuration is in accord with the preceeding works.[31,32] Despite different attempts, i.e. synthesis with the Pt(SEt$_2$)Cl$_2$ trans isomer, synthesis with the magnesium salt of BrPhpz, or photochemical or thermal isomerization, invariably only one isomer was obtained.

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Registry No. I, 88821-71-9; II, 109284-54-0; III, 100012-12-2; IV, 109284-55-1; V, 109284-56-2; VI, 109306-87-8; *cis*-[Pt(SEt$_2$)$_2$Cl$_2$], 15442-57-6; *trans*-PtCl$_2$(Et$_2$S)$_2$, 15337-84-5; Pt(bpy)$_2$(PF$_6$)$_2$, 109284-58-4; 2-(2-bromophenyl)pyridine, 109306-86-7; 1-(2-bromophenyl)-pyrazole, 87488-84-4; 2-(2-thienyl)pyridine, 3319-99-1; 2-(3-thienyl)-pyridine, 21298-55-5; 1-(2-thienyl)pyrazole, 74990-30-0; 2-(3-(trimethylsilyl)-2-thienyl)pyridine, 51459-67-7; 1-phenylpyrazole magnesium salt, 109284-57-3; (4-(2-(2-thienyl)pyridinyl))lithium, 85594-03-2; platinum-195, 14191-88-9.

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