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SYNTHESIS AND CHARACTERIZATION OF DOUBLE CYCLOPALLADATED COMPLEXES OF SCHIFF BASES AND AZINE—OXIDATIVE ADDITION OF ARYL–HALOGEN BOND

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Abstract—The oxidative addition of aryl–halogen bonds of Schiff bases (2-ClC_6H_4CH=N—CH_2—)$_2$ (**1**), (2-BrC_6H_4CH=N—CH_2—)$_2$ (**2**), 1,4-(2-BrC_6H_4CH=N—)$_2C_6H_4$ (**3**), 4,4′-(2-BrC_6H_4CH=N—C_6H_4)$_2$ (**4**) and the azine (2-BrC_6H_4CH=N—)$_2$ (**5**) to $Pd(dba)_2$ has been carried out in benzene. Insoluble halogeno-bridged polymeric complexes [{Pd(C_6H_4CH=N—CH_2—)Cl}$_n$] (**1a**), [{Pd(C_6H_4CH=N—CH_2—)Br}$_n$] (**2a**), [1,4-{BrPd(C_6H_4CH=N—C_6H_4—N=CHC_6H_4)PdBr}$_n$] (**3a**), [4,4′-{Pd(C_6H_4CH=N—C_6H_4)Br}$_n$] (**4a**) and [{Pd(C_6H_4CH=N—)Br}$_n$] (**5a**) were formed. The bridge-splitting reactions of halogeno-bridged complexes were studied with different ligands like triphenylphosphine, triethylphosphite, 4-picoline, diethyldithiocarbamate and *N*-(2-hydroxy)benzylideneamine. All the double cyclopalladated complexes obtained were analysed by means of ^1H NMR and ^{13}C NMR spectroscopy.

Cyclopalladation is an important area of current interest in organometallic chemistry.[1] The cyclopalladated complexes are widely used in diverse areas like organic synthesis,[2] homogeneous catalysis,[3] liquid crystals,[4] photochemistry[5] etc. Different types of nitrogen-containing ligands like amines, azines, hydrazones, oximes and Schiff bases have been used to synthesize cyclopalladated complexes and several methods have been employed to synthesize. Oxidative addition was found to be an elegant method and has been used to synthesize cyclopalladated complexes of amines,[6] hetrocycles[7] and Schiff bases.[8] Among the different ligands, Schiff bases are found to be suitable ligands for cyclopalladation reactions. Several reports are available on monopalladated complexes of Schiff bases,[9] but only scanty reports have appeared on doubly cyclopalladated complexes of Schiff bases.[10] To our knowledge, the simple Schiff base (C_6H_4CH=N—CH_2—)$_2$ has not been used for cyclopalladation reactions so far, but has been used with $Pd(OAc)_2$ as a catalyst for the cyclization reaction instead.[11] Moreover, it has been used as a bidentate ligand in coordination chemistry.[12] Here we report the preparation of doubly cyclopalladated complexes of different Schiff bases (2-ClC_6H_4CH=N—CH_2—)$_2$ (**1**), (2-BrC_6H_4CH=N—CH_2—)$_2$ (**2**), 1,4-(2-BrC_6H_4CH=N—)$_2C_6H_4$ (**3**), (2-BrC_6H_4CH=N—C_6H_4)$_2$ (**4**) and the azine (2-BrC_6H_4CH=N—)$_2$ (**5**) using $Pd(dba)_2$ as starting material under oxidative addition conditions.

EXPERIMENTAL

Solvents were purified by the standard method.[13] $Pd(dba)_2$ was prepared from Na_2PdCl_4.[14] Elemental analyses were carried out in a Heraeus CHN-O rapid elemental analyser. The IR spectra in the range of 4000–400 cm^{-1} were recorded as KBr discs using a Shimadzu IR-470 spectrophotometer. IR spectra in the range of 400–50 cm^{-1} were recorded

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as polyethylene discs using a Bruker IFS 66v spectrophotometer. ^{1}H NMR and ^{13}C NMR were recorded using a JEOL-JNM-GSX400 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were taken in $CDCl_3$ solution with tetramethylsilane as internal standard. The Schiff bases and azine were prepared by refluxing two equivalents of 2-bromobenzaldehyde with one equivalent of amine or hydrazine in ethanol for 2 h. *N*-(2-Hydroxy) benzylidene-n-butylamine and *N*-(2-hydroxy) benzylideneaniline were prepared by refluxing one equivalent of salicylaldehyde with one equivalent of appropriate amine in ethanol for 1 h.

Synthesis of complexes

Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)Cl}$_n$] (**1a**). The Schiff base **1** (61 mg, 0.2 mmol) was refluxed with Pd(dba)$_2$ (230 mg, 0.4 mmol) in 30 cm^3 of benzene under N_2 for 2 h. The chloro-bridged complex **1a** was filtered, washed with benzene and dried *in vacuo* (90 mg).

Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)Br}$_n$] (**2a**). The Schiff base **2** (78.8 mg, 0.2 mmol) was stirred with Pd(dba)$_2$ (230 mg, 0.4 mmol) at 75°C in 30 cm^3 of benzene for 5 min under N_2. The bromo-bridged complex **2a** formed was filtered, washed with benzene and dried *in vacuo* (110 mg). Compounds **3a**, **4a** and **5a** were prepared similarly.

Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)Cl(PPh$_3$)}$_2$] (**1b**). The chloro-bridged polymeric complex **1a** (104 mg) was stirred with triphenylphosphine (105 mg, 0.4 mmol) in 5 cm^3 of $CHCl_3$ for 2 h. The resultant clear solution was filtered and concentrated. The residue obtained was chromatographed on a column packed with silica gel. Elution with dichloromethane–methanol (1%) gave the white product **1b** (160 mg, 76%). Complexes **2b** and **3b** were made similarly.

Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)Cl(P(OEt)$_3$)}$_2$] (**1c**). The chloro-bridged polymeric complex **1a** (104 mg) was stirred with triethylphosphite (66.4 mg, 0.4 mmol) in 5 cm^3 of $CHCl_3$ for 2 h. The resultant clear solution was filtered, concentrated and chromatographed on a column packed with silica gel. Elution with chloroform–methanol (1%) gave the pale yellow product **1c** (130 mg, 76%). Complexes **2c**, **3c**, **4c** and **5c** were prepared similarly from the respective bromo-bridged complexes.

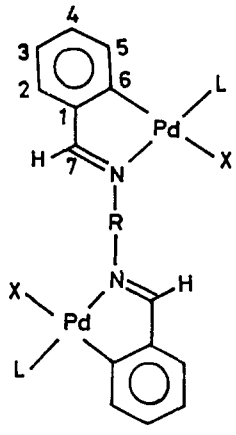
Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)Cl(4-CH$_3$C$_5$H$_5$N)}$_2$] (**1d**). The chloro-bridged complex **1a** (104 mg) was stirred with 4-picoline (370 mg, 0.4 mmol) in 5 cm^3 of $CHCl_3$ for 2 h. The clear solution obtained was filtered, concentrated and chromatographed on a column packed with silica gel. Elution with chloroform–methanol (2%) gave the pale yellow product **1d**. It was recrystallized from $CHCl_3$–MeOH (105 mg, 74%). Complex **2d** was prepared similarly from **2a**.

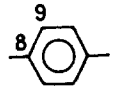
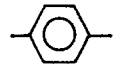
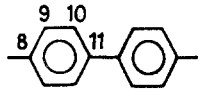
Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)(S$_2$C=NEt$_2$)}$_2$] (**1e**). The bromo-bridged polymeric complex **2a** (61 mg) was stirred with sodium diethyldithiocarbamate (45 mg, 0.2 mmol) in 5 cm^3 methanol for 5 h. The product formed was filtered, washed with methanol and chromatographed on silica gel. Elution with $CHCl_3$ gave a yellow coloured product. Complex **1e** that obtained was recrystallized from $CHCl_3$–MeOH (60 mg, 80%). Complex **5e** was prepared similarly from **5a**.

Preparation of [{Pd(C$_6$H$_4$CH=N—CH$_2$—)(2-O-C$_6$H$_4$CH=N—C$_4$H$_9$)}$_2$] (**1f**). To the bromo-bridged complex **2a** (90 mg) in 5 cm^3 of methanol was added a clear solution of *N*-(2-hydroxy) benzylidene-n-butylamine (53 mg, 0.3 mmol) and sodium hydroxide (12 mg, 0.3 mmol) in 5 cm^3 of methanol with stirring. The suspension was stirred for 10 h. The product was filtered, washed with methanol and chromatographed on a column packed with silica gel. Elution with dichloromethane–methanol (1%) gave a bright yellow product after evaporation. Product **1f** was recrystallized from CH_2Cl_2–MeOH (90 mg, 76%). Complex **1g** was prepared similarly from **2a** using *N*-(2-hydroxy)benzylideneaniline.

RESULTS AND DISCUSSION

The oxidative addition reaction of Pd(dba)$_2$ with the 2-chloro-substituted Schiff base **1** was carried out in refluxing benzene. The insoluble complex **1a** formed was found to be a chloro-bridged polymeric complex. The IR spectrum shows two bands at 297 and 261 cm^{-1}, suggesting a chloro-bridged complex (Table 1). Similar oxidative addition reactions were carried out with the 2-bromo-substituted Schiff bases **2**, **3**, **4** and azine **5**. The complexes **2a**, **3a**, **4a** and **5a** formed were found to be insoluble bromo-bridged complexes. The IR spectra of these complexes exhibit two bands corresponding to Pd—Br in the far-IR region. The oxidative addition reaction was slow with 2-chloro-substituted Schiff base **1** due to the high C—Cl bond energy (96 kcal mol^{-1}). However, oxidative addition occurred much faster than **1** with Schiff bases **2**, **3** and **4** and azine **5**, which is attributed to a lower bond energy of the C—Br bond (81 kcal mol^{-1}). Vila *et al.* prepared soluble bromo-bridged tetranuclear complexes from substituted 1,4-(C$_6$H$_5$CH=N—)$_2$C$_6$H$_4$



	R	L	X
1b	$-CH_2-CH_2-$	PPh_3	Cl
1c	$-CH_2-CH_2-$	$P(OEt)_3$	Cl
2b	$-CH_2-CH_2-$	PPh_3	Br
2c	$-CH_2-CH_2-$	$P(OEt)_3$	Br
3b		PPh_3	Br
3c		$P(OEt)_3$	Br
4c		$P(OEt)_3$	Br

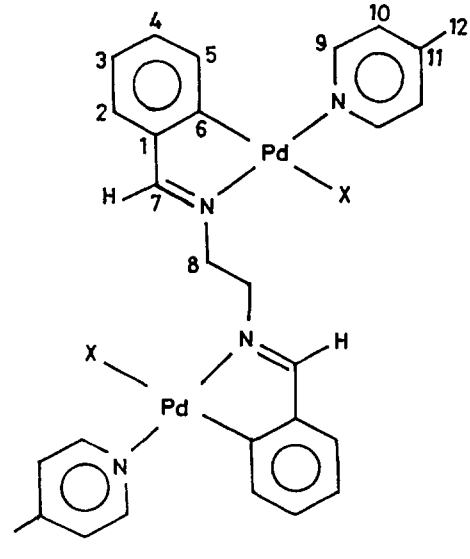
using $Pd(OAc)_2$ in refluxing acetic acid followed by a metathesis reaction with NaBr.[10] In contrast, its 2-bromo analogue **3**, in oxidative addition conditions, gave rise to insoluble bromo-bridged polymeric complex **3a**.

The bridge-splitting reactions with the polymeric complexes **1a–5a** were carried out with monodentate ligands like triphenylphosphine, triethylphosphite and 4-picoline. Complex **1a** gave **1b** with triphenylphosphine. Similarly, **2b** and **3b** were obtained from **2a** and **3a**, respectively. Complexes **1b**, **2b** and **3b** are less soluble in common organic solvents. The soluble complexes **1c–5c** were prepared from **1a–5a** using triethylphosphite. Similarly, **1d** and **2d** were prepared from **1a** and **2a** using 4-picoline as the bridge-splitting ligand.

The bridge-splitting reactions were also carried out with bidentate ligands like diethyldithiocarbamate, *N*-(2-hydroxy)benzylidene-n-butylamine and *N*-(2-hydroxy)benzylideneaniline. The reaction of **2a** with diethyldithiocarbamate gave the yellow complex **1e**. Complex **5e** was made similarly from **5a**. The reactions of ligands *N*-(2-hydroxy) benzylidene-n-butylamine and *N*-(2-hydroxy) benzylideneaniline carried out with **2a** gave **1f** and **1g**, respectively.

In all the cyclopalladated complexes, the asymmetric stretching band of C=N is shifted to lower wavenumber compared to the free ligand. This shift is due to the coordination of the nitrogen atom to the metal atom.[9,15] The ^1H NMR spectra show that the HC=N proton resonance is shifted to high field in all cyclopalladated Schiff base complexes, compared to the free ligand, due to a decrease of double bond character of C=N after complexation.[16]

It is a well known fact that the HC=N proton resonances of azines are shifted to lower field after complexation. This shift to low field was explained on the basis of the close proximity of the HC=N proton to the metal atom.[17] However in complexes **5c** and **5e**, in contrast to earlier observations, the HC=N proton is shifted to high field. The HC=N proton resonates as a doublet at δ 8.88 [J(PH) =



1d X = Cl
2d X = Br

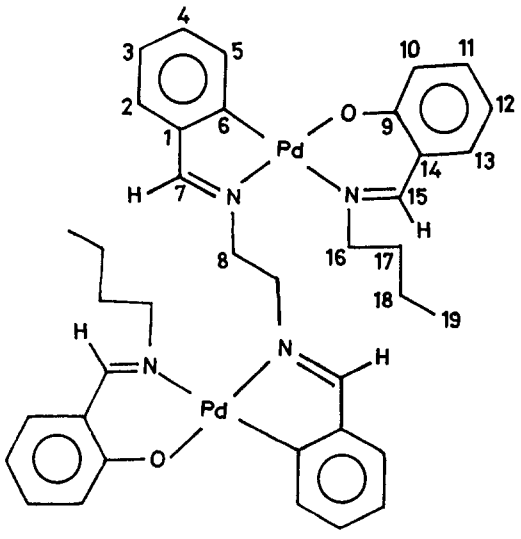
Table 1. Elemental and IR spectral data of the complexes[a]

Complex	Colour	Analytical data			IR data		
		C	H	N	ν(C=N)	ν(Pd—X^t)	ν(Pd—X^b)
1	White				1635		
1a	Light grey				1610		261, 297
1b	White	60.3	4.2	2.8	1625	315	
		(59.9)	(4.3)	(2.7)			
1c	Light yellow	39.3	5.2	3.3	1625	321	
		(39.6)	(5.2)	(3.3)			
1d	Light yellow	47.6	4.0	7.7	1613	320	
		(47.8)	(4.0)	(8.0)			
1e	Yellow	41.7	4.5	7.4	1612		
		(42.0)	(4.6)	(7.5)			
1f	Yellow	56.9	5.3	7.2	1612		
		(57.1)	(5.3)	(7.0)			
1g	Yellow	60.2	4.2	6.8	1619		
		(60.1)	(4.1)	(6.7)	1593		
2	White				1632		
2a	Light grey				1619		164, 196
2b	White	55.3	3.9	2.6	1625	178	
		(55.2)	(3.9)	(2.5)			
2c	Light yellow	35.8	4.6	2.9	1625	171	
		(35.8)	(4.7)	(3.0)			
2d	Light yellow	42.0	3.5	7.0	1610	168	
		(41.4)	(3.6)	(7.1)			
3	Yellow				1612		
3a	Light yellow				1594		161, 197
3b	Yellow	7.0	3.7	2.4	1600	177	
		(57.0)	(3.8)	(2.4)			
3c	Yellow	39.4	4.4	2.8	1600	177	
		(38.9)	(4.5)	(2.8)			
3e	Yellow	45.6	4.3	6.9	1584		
		(45.5)	(4.3)	(7.2)			
4	Yellow				1616		
4a	Light yellow				1606		173, 193
4c	Yellow	43.6	4.4	2.8	1606	170	
		(43.9)	(4.6)	(2.6)			
5	Yellow				1616		
5a	Yellow				1593		146, 204
5c	Yellow	34.3	4.5	2.9	1600	183	
		(34.3)	(4.4)	(3.1)			
5e	Yellow	39.9	4.2	7.7	1605		
		(40.3)	(4.2)	(7.8)			

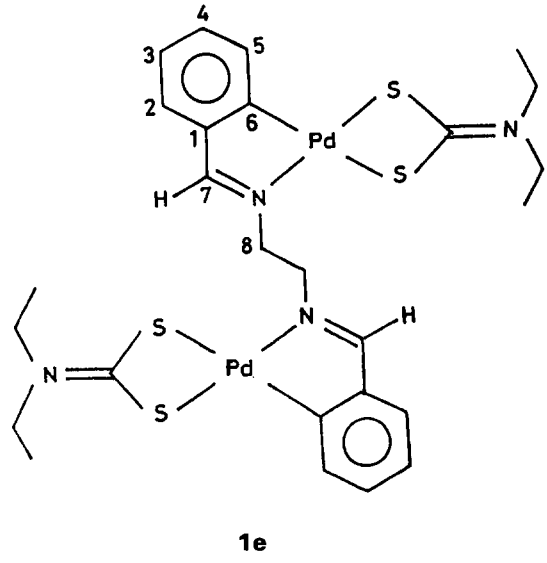
[a] Calculated values are given in parentheses; IR spectral values are in cm^{-1}; b, bridged Pd—X bond; t, terminal Pd—X bond.

6.72 Hz] in **5c** and as a singlet at δ 8.9 in **5e**. The HC=N proton of the free ligand resonates at δ 9. The paramagnetic anisotropy of the metal on the HC=N proton and reduction of the double bond character of C=N after complexation are opposing effects. In complexes **5c** and **5e** the slight upfield shift of the HC=N proton shows that the effect of paramagnetic anisotropy of the metal on the HC=N proton is less than the effect of reduction of the double bond character of C=N.

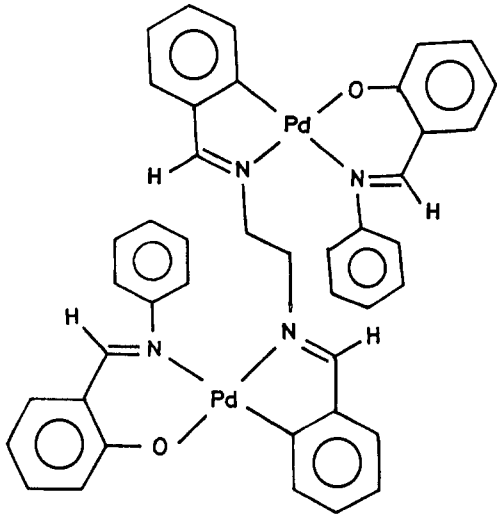
The IR spectrum of complex **1f** shows only one strong band at 1612 cm^{-1} corresponding to both C=N bonds. However, two bands appeared in complex **1g** at 1619 and 1593 cm^{-1}. The former corresponds to the C=N group (C^7) belonging to the backbone of the complex; the latter cor-



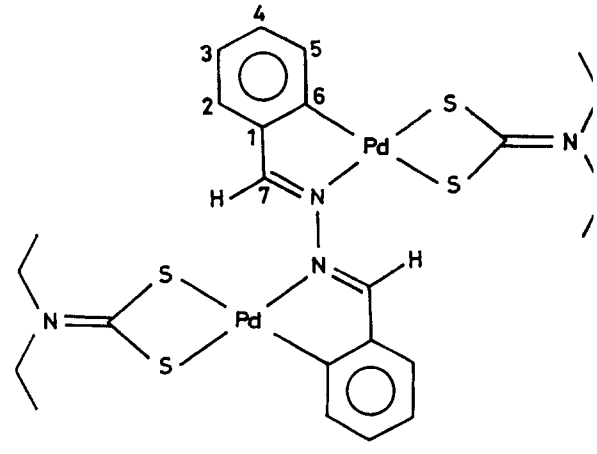
1f



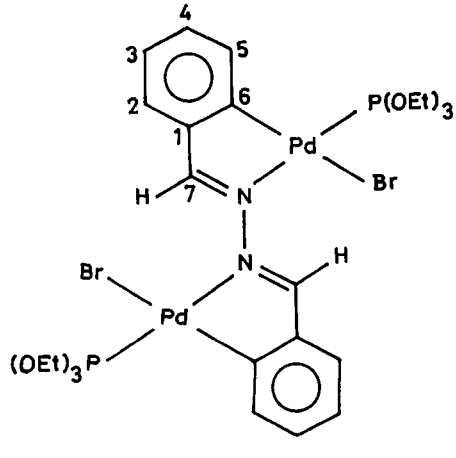
1e



1g



5e



5c

Table 2. ^{1}H NMR and ^{13}C NMR spectral data of the complexes[a]

1d ^{1}H NMR: δ 2.4 (s, 3H, H^{12}), 4.4 (s, 2H, H^8), 6.2 (d, 1H, H^5), 6.93 (dt, 1H, H^3), 7.01 (dt, 1H, H^4), 7.27 (m, 3H, H^2, H^{10}), 8.3 (s, 1H, H^7), 8.7 (d, 2H, H^9).
^{13}C NMR: δ 21.25 (q, C^{12}), 59.93 (t, C^8), 124.56 (d, C^3), 126.38 (d, C^{10}), 127.94 (d, C^4), 130.43 (d, C^2), 131.85 (d, C^5), 146.65 (s, C^1), 150.23 (s, C^{11}), 152.37 (d, C^9), 158.12 (s, C^6), 178.52 (d, C^7).

1e ^{1}H NMR: δ 1.31 (t, 3H, CH_3), 1.35 (t, 3H, CH_3), 3.85 (q, 4H, CH_2), 4.12 (s, 2H, H^8), 6.98 (m, 1H, H^4), 7.07 (m, 2H, H^2, H^3), 7.25 (m, 1H, H^5), 8.2 (s, 1H, H^7).
^{13}C NMR: δ 12.42 (q, CH_3), 12.52 (q, CH_3), 44.64 (t, CH_2), 45.60 (t, CH_2), 60.35 (t, C^8), 124.10 (d, C^3), 128.26 (d, C^4), 130.68 (d, C^2), 133.15 (d, C^5), 146.61 (s, C^1) 161.38 (s, C^6), 177.56 (d, C^7), 209.18 (s, C^9).

1f ^{1}H NMR: δ 0.9 (t, 3H, H^{19}), 1.4 (m, 2H, H^{18}), 1.86 (m, 2H, H^{17}), 4.00 (t, 2H, H^{16}), 4.3 (s, 2H, H^8), 6.52 (t, 1H, H^{12}), 6.85 (d, 1H, H^{11}), 7.17 (dd, 1H, H^{13}), 7.27 (m, 2H, H^{10}, H^5), 6.91 (t, 1H, H^3), 7.00 (dd, 1H, H^2), 7.05 (dt, 1H, H^4), 7.80 (s, 1H, H^{15}), 7.95 (s, 1H, H^7).
^{13}C NMR: δ 13.84 (q, C^{19}), 19.76 (t, C^{18}), 35.78 (t, C^{17}), 56.86 (t, C^{16}), 63.45 (t, C^8), 113.80 (d, C^{10}), 121.72 (d, C^{12}), 122.22 (s, C^{14}), 123.86 (d), 127.52 (d), 129.84 (d), 134.04 (d), 134.14 (d), 134.74 (d, aromatic), 147.1 (s, C^1), 157.27 (s, C^6), 164.59 (d, C^{15}), 167.52 (s, C^4), 178.22 (d, C^7).

2c ^{1}H NMR: δ 1.37 (t, 9H, CH_3), 4.28 (m, 8H, H^8, CH_2), 7.10 (m, 2H, H^2, H^3), 7.23 (d, 1H, H^5), 7.60 (t, 1H, H^4), 8.35 [d, ^4J(PH) = 10 Hz, 1H, H^7].
^{13}C NMR: δ 16.13 (q, CH_3), 57.94 (t, CH_2), 62.71 (t, C^8), 124.94 (d, C^3), 128.95 (d, C^2), 131.01 [d, J(PC) = 6.1 Hz, C^4], 136.68 [d, J(PC) = 9.1 Hz, C^5], 147.66 [s, J(PC) = 3.1 Hz, C^1], 156.72 (s, C^6), 178.52 [d, J(PC) = 6.1 Hz, C^7].

3c ^{1}H NMR: δ 1.37 (t, 9H, CH_3), 4.29 (m, 6H, CH_2), 7.20 (m, 2H, H^2, H^3), 7.32 (s, 2H, H^9), 7.46 [dd, ^4J(PH) = 6.65 Hz, 1H, H^5], 7.74 (t, 1H, H^4), 8.27 [d, ^4J(PH) = 9.35 Hz, 1H, H^7].
^{13}C NMR: δ 16.05 (q, CH_3), 62.96 (t, CH_2), 123.54 (d, C^9), 125.21 (d, C^2), 130.0 (d, C^3), 131.89 [d, J(PC) = 6.1 Hz, C^4], 136.98 [d, J(PC) = 9.1 Hz, C^5], 147.69 [s, J(PC) = 6.0 Hz, C^1], 147.75 (s, C^8), 158.89 [s, J(PC) = 7.6 Hz, C^6], 176.74 [d, J(PC) = 6.1 Hz, C^7].

4c ^{1}H NMR: δ 1.37 (t, 9H, CH_3), 4.30 (m, 6H, CH_2), 7.22 (m, 2H, H^2, H^3), 7.38 (d, 2H, H^9), 7.45 (d, 1H, H^5), 7.62 (d, 2H, H^{10}), 7.75 (t, 1H, H^4), 8.25 [d, ^4J(PH) = 9.6 Hz, 1H, H^7].
^{13}C NMR: δ 16.06 (q, CH_3), 62.99 (t, CH_2), 124.18 (d, C^{10}), 125.17 (d, C^3), 126.79 (d, C^9), 129.83 (d, C^2), 131.88 [d, J(PC) = 6.1 Hz, C^4], 137.1 [d, J(PC) = 9.1 Hz, C^5], 139.31 (s, C^{11}), 147.77 [s, J(PC) = 3.1 Hz, C^1], 148.27 (s, C^8), 159.03 (s, C^6), 176.34 [d, J(PC) = 6.1 Hz, C^7].

5c ^{1}H NMR: δ 1.36 (t, 9H, CH_3), 4.28 (m, 6H, CH_2), 7.17 (m, 2H, H^2, H^3), 7.52 [dd, ^4J(PH) = 6.72 Hz, 1H, H^5], 7.65 (t, 1H, H^4), 8.88 [d, ^4J(PH) = 6.72 Hz, 1H, H^7].
^{13}C NMR: δ 16.03 (q, CH_3), 63.15 (t, CH_2), 125.41 (d, C^3), 130.97 (d, C^2), 131.75 [d, J(PC) = 7.5 Hz, C^4], 136.68 [d, J(PC) = 10.7 Hz, C^5], 143.21 (s, C^1), 157.82 (s, C^6), 174.56 (d, C^7).

5e ^{1}H NMR: δ 1.29 (t, 3H, CH_3), 1.35 (t, 3H, CH_3), 3.83 (m, 4H, CH_2), 7.11 (dt, 2H, H^3, H^4), 7.16 (dd, 1H, H^2), 7.48 (dd, 1H, H^5), 8.90 (s, 1H, H^7).
^{13}C NMR: δ 12.43 (q, CH_3), 12.58 (q, CH_3), 44.64 (t, CH_2), 45.55 (t, CH_2), 124.76 (d, C^3), 130.31 (d, C^4), 131.65 (d, C^2), 133.00 (d, C^5), 142.59 (s, C^1), 159.96 (s, C^6), 171.60 (d, C^7), 208.18 (s, C^8).

[a] Chemical shifts in ppm (δ) with respect to internal $SiMe_4$. See structures for numbering sequence. Chemical shifts (δ) due to CH=N of free ligand **1** = 8.69; **2** = 8.65; **3** = 8.9; **4** = 8.92; **5** = 9.0.

responds to the C=N group of *N*-(2-hydroxy) benzylideneaniline. The asymmetric C=N streching frequencies of the ligands *N*-(2-hydroxy) benzylidene-n-butylamine and *N*-(2-hydroxy) benzylideneaniline are 1632 and 1610 cm^{-1}, respectively.

The ^{1}H NMR spectrum of complex **1f** shows two singlets for two HC=N protons. The HC=N proton (H^7) appears at δ 7.95. The other CH=N proton, belonging to *N*-(2-hydroxy)benzylidene-n-butylamine, appears at δ 7.8. In the free ligands, the HC=N protons resonate at δ 8.65 and 8.30, respectively.

A strong band due to the asymmetric stretching frequency of the C=N bond at *ca* 1510 cm^{-1} in complexes **1e** and **5e** shows considerable double bond character between the C—N bond of the diethyldithiocarbamate moiety. This hinders free rotation around the C—N bond. The ^{1}H NMR spectrum of complex **1e**, two triplets at δ 1.31 and 1.35, suggests that the methyl groups are not magnetically equivalent; however, a quartet at δ 3.85 for the methylene groups suggests that they are magnetically equivalent.[18] In contrast to complex **1e**, the ^{1}H NMR spectrum of the azine complex **5e** suggests that the ethyl groups are not magnetically equivalent, which is inferred from two triplets at δ 1.29 and 1.35 for the methyl groups and a multiplet at δ 3.83 for the methylene groups.[19] From the ^{13}C NMR spectra of complexes **1e** and **5e**, it is inferred

that both methyl and methylene carbon atoms are not magnetically equivalent. The peak around 160 ppm in the ^{13}C NMR spectra for all metallated complexes is typical of a metallated carbon atom.

The proton adjacent to the metallated carbon atom of complex **1d** is shifted to high field due to diamagnetic shielding of 4-picoline. Similar shielding is observed in dimetallated amine complexes[20] and monometallated binuclear complexes of Schiff bases and amines.[21] The remaining resonances have been assigned accordingly (Table 2).

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