# Synthesis and characterization of a bidentate chelating diisonitrile ligand with two thioethereal sulfurs in a bridging group and its copper(I), rhodium(I) and palladium(II) complexes

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## Abstract

The diisonitrile ligand (L) has been synthesized in five reaction steps from t-butylbenzene with an overall yield of 7.3%. The reaction of palladium(II) chloride with L leads to the palladium(II) complex, $PdLCl_2$, whereas the rhodium(I) complexes, $RhL_2Cl$ and $RhL_2BF_4$, and the copper(I) complex, $CuL_2BF_4$, are prepared by ligand exchange reactions. These complexes were investigated by means of mass, infrared, nuclear magnetic resonance (NMR) and electronic spectra, as well as molar conductances. Judging from the molar conductances of the $RhL_2Cl$, $RhL_2BF_4$ and $CuL_2BF_4$ complexes, tetrafluoroborate and chloride anions are ionized in acetonitrile. This is also supported by mass spectral data. The strong band at 2100 $cm^{-1}$ is assigned to the $N \equiv C$ stretching mode. This band shifts to higher frequency upon metal coordination because of the inductive effect produced by the positive charge of the metal ions. This shift increases with increasing charge on the complex. The methylene proton signals of the benzyl group and the bridging group in the ligand are shifted slightly downfield on formation of the complexes. Since the magnitude of the shift is approximately proportional to the oxidation number in the metal complexes, the oxidation number could be distinguished by proton NMR studies of the methylene groups. These results indicate that the $N \equiv C$ group in the ligand serves as a σ-donor and the thioethereal sulfur in the bridging group is not coordinated to the metal atoms. It is surprising that L does not coordinate through the sulfur atoms rather than the isonitriles, because the S-coordinated form would have a stable five-membered-ring structure and the isonitrile coordination gives a fifteen-membered-ring structure.

*Keywords:* Copper complexes; Rhodium complexes; Palladium complexes; Bidentate isonitrile complexes; Chelate complexes

## 1. Introduction

Although metal complexes of monodentate isonitriles have been widely investigated for preparing carbene complexes [1] and for forming C–C bonds [2], the coordination chemistry of bidentate diisonitriles is relatively unexplored with respect to the formation of binuclear or polymeric metal complexes. Angelici et al. provided the first definitive evidence for the formation of chelate complexes by employing bidentate aromatic diisonitriles [3–8]. For example, it was reported that these ligands are ideally suited to chelation with the donor groups at an angle of 90° to one another, and that they form chelate complexes with the large thirteen-membered chelate rings [3–8]. These ligands have four coordination sites, namely two ethereal oxygens in the

bridging group and two carbene carbons in the isonitrile groups, as judged by a Corey–Pauling–Koltum model, but the latter is coordinated only to metals.

It is commonly observed that the coordination bond between sulfur donors and low-valent transition metals is much stronger than that between oxygen donors and low-valent transition metals. Hence we synthesized a ligand with two isonitrile groups and two thioethereal sulfurs in the bridging group, that is, 1,2-bis(4-t-butyl-2-isocyanobenzylthio)ethane (L) (Scheme 1), in the present work. This work presents part of a more usual
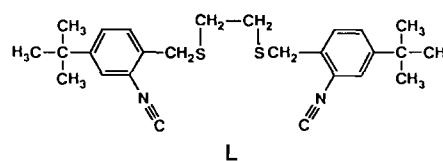


Scheme 1. Structure of the diisonitrile ligand L.

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investigation into the synthesis of a diisonitrile ligand. We report in detail the formation of four complexes derived from this ligand with low-valent transition metal complexes by ligand-exchange reaction. We characterized the spectral properties of L and its metal complexes with the aid of mass spectroscopy (MS), vibrational spectroscopy, electronic spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, as well as conductivity measurements.

## 2. Experimental

### 2.1. Physical measurements

EI mass spectra (EI-MS) at 70 eV, utilizing a direct inlet system for the diisonitrile ligand, its starting materials and the palladium(II) complex, and FAB mass spectra in a glycerine matrix for the rhodium(I) and copper(I) complexes were carried out with a JEOL JMX-DX 300 gas chromatograph–mass spectrometer. Infrared (IR) spectra in the region 400–4000 cm$^{-1}$ were obtained on a Hitachi 260-30 spectrophotometer at room temperature using the KBr disk method. $^1$H NMR measurements were taken on a JEOL JNM-FX 60 spectrometer operating in the Fourier transform mode. The NMR spectra were run in chloroform-d$_1$ and dimethyl sulfoxide-d$_6$, and chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard. All melting points were observed using a Yanaco MP-500D micro melting point apparatus (hot-plate type) and were not corrected. Elemental analyses were determined with a Yanaco CHN Corder MT-3. Conductivity measurements were performed on acetonitrile solutions of the complexes thermostatted to 25.0±0.2 °C with a Coolnics Thermo-Bath (model CTE-310). Conductivities were measured with a TOA Electronics CM-20E instrument. Ultraviolet and visible spectra covering the 220–700 nm range were recorded on a Shimadzu UV 200S double-beam spectrophotometer for methanol solutions at room temperature.

### 2.2. Synthesis of the bidentate diisonitrile ligand

#### 2.2.1. 4-t-Butylbenzyl chloride (1) [9]

A mixture of t-butylbenzene (83.23 g, 620 mmol), paraformaldehyde (39.0 g), glacial acetic acid (95.55 g), phosphoric acid (85%, 278.0 g) and hydrochloric acid (35%, 152.4 g, 1.50 mmol) was kept at 80–85 °C for two days with vigorous stirring. The organic layer was separated from the reaction solution and was distilled under nitrogen atmosphere at 102.2–104.0 °C (7 torr) to give a colorless viscous liquid; yield 60.4 g (53.5%). IR data (neat) cm$^{-1}$: 2950 (C–H str., s), 1275 (C–Cl str., s), 760 (out-of-plane C–H bend., s). EI-MS: m/z (relative intensity) 184 (6.01, [M+2]$^+$), 182 (16.6,

M$^+$), 169 (34.2, [M+2-CH$_3$]$^+$), 167 (100, [M-CH$_3$]$^+$), 147 (32.6, [M-Cl]$^+$) (molecular weight 182.70). $^1$H NMR (chloroform-d$_1$, TMS): δ 1.29 (9H, s, (CH$_3$)$_3$C–), 4.49 (2H, s, -CH$_2$-), 7.31 (4H, s, aromatic) ppm. Anal. Calc. for C$_{11}$H$_{15}$Cl: C, 72.32; H, 8.28. Found: C, 72.55; H, 8.48%.

#### 2.2.2. 4-t-Butyl-2-nitrobenzyl chloride (2) [10]

A mixture of nitric acid (70%, sp. gr. 1.42, 5.0 ml, 113 mmol), sulfuric acid (96%, 12.0 ml) and water (3.0 ml) was maintained at 0–10 °C; to it, 1 (11.0 ml, 60 mmol) was added dropwise. After the reaction mixture was stirred vigorously at 5–10 °C for 6 h, benzene (300 ml) and water (300 ml) were added. The organic layer was separated from the reaction solution and washed five times with water (100 ml). Benzene was removed using an evaporator, and the product was distilled under nitrogen atmosphere at 153.0–155.0 °C (4 torr) to produce a viscous yellow liquid; yield 10.51 g (81.1%). IR data (neat) cm$^{-1}$: 2952 (C–H str., s), 1540, 1360 (N–O str., s), 1260 (C–Cl str., m). EI-MS: m/z (relative intensity) 229 (10.6, [M+2]$^+$), 227 (29.6, M$^+$), 214 (87.7, [M+2-CH$_3$]$^+$), 212 (100, [M-CH$_3$]$^+$) (molecular weight 227.69). $^1$H NMR (chloroform-d$_1$, TMS): δ 1.35 (9H, s, (CH$_3$)$_3$C–), 4.92 (2H, s, -CH$_2$-), 7.35–8.07 (3H, m, aromatic) ppm. Anal. Calc. for C$_{11}$H$_{14}$ClNO$_2$: C, 58.03; H, 6.20; N, 6.15. Found: C, 58.31; H, 6.33; N, 6.33%.

#### 2.2.3. 1,2-Bis(4-t-butyl-2-nitrobenzylthio)ethane (3) [11]

A mixture of 1,2-ethanedithiol (2.0 ml, 25 mmol), 2 (11.35 g, 50 mmol) and methanol (10.0 ml) was stirred at about 50 °C for 1 h, while ammonia gas was continuously bubbled through it. After the reaction mixture was allowed to stand at room temperature, benzene (100 ml) was added to it and the insoluble material was removed by filtration. The filtrate was concentrated to about 10 ml under reduced pressure. The concentrate was chromatographed on silica gel (150×40 mm, 60–80 mesh, Kanto Chemical) and eluted with dichloromethane. The second compound was collected, dichloromethane was removed on a rotary evaporator, and a highly viscous yellow oil was obtained; yield 9.87 g (82.9%). IR data (neat) cm$^{-1}$: 2950, 2860 (C–H str., s), 1540, 1345 (N–O str., s), 680 (C–S str., m). EI-MS: m/z (relative intensity) 477 (0.60, [M+1]$^+$), 476 (2.48, M$^+$), 475 (1.75, [M-H]$^+$), 286 (13.5, [M+2-(C$_{11}$H$_{14}$NO$_2$)]$^+$), 285 (29.1, [M+1-(C$_{11}$H$_{14}$NO$_2$)]$^+$), 284 (79.8, [M-(C$_{11}$H$_{14}$NO$_2$)]$^+$), 193 (47.7, [M+1-(C$_{13}$H$_{18}$NO$_2$S$_2$)]$^+$), 192 (100, [M-(C$_{13}$H$_{18}$NO$_2$S$_2$)]$^+$) (molecular weight 476.65). $^1$H NMR (chloroform-d$_1$, TMS): δ 1.34 (18H, s, (CH$_3$)$_3$C–), 2.63 (4H, s, -SCH$_2$-CH$_2$S-), 4.03 (4H, s, Ar–CH$_2$S-), 7.40–7.97 (6H, m, aromatic) ppm. Anal. Calc. for C$_{24}$H$_{32}$N$_2$O$_4$S$_2$: C, 60.48; H, 6.77; N, 5.88. Found: C, 60.25; H, 6.86; N, 6.01%.

### 2.2.4. 1,2-Bis(4-t-butyl-2-aminobenzylthio)ethane (4) [12]

A mixture of zinc (10.0 g), 3 (0.224 g, 0.47 mmol), calcium chloride (1.40 g), ethanol (200 ml) and water (50 ml) was heated under reflux for 24 h with vigorous stirring. The hot mixture was filtered off and to it was added water (400 ml) until the solution became whitely turbid. The reaction mixture was heated at 50 °C for 1 h and cooled with ice water. The crystalline product was isolated by filtration, washed three times with water (10 ml) and dried in vacuo to give fine white crystals; yield 0.158 g (80.8%), m.p. 88.0–92.0 °C. IR data (KBr disk) $cm^{-1}$: 3410, 3300 (N–H str., m), 2960 (C–H str., s), 1605 (N–H bend., s). EI-MS: $m/z$ (relative intensity) 417 (2.59, $[M+1]^+$), 416 (6.54, $M^+$), 255 (3.06, $[M+1-(C_{11}H_{16}N)]^+$), 254 (11.2, $[M-(C_{11}H_{16}N)]^+$), 163 (15.5, $[M+1-(C_{13}H_{20}NS_2)]^+$), 162 (100, $[M-(C_{13}H_{20}NS_2)]^+$) (molecular weight 416.69). $^1H$ NMR (chloroform-$d_1$, TMS): $\delta$ 1.27 (18H, s, $(CH_3)_3C-$), 2.84 (4H, s, $-SCH_2-CH_2S-$), 3.55 (4H, s, Ar–$CH_2S-$), 3.75 (4H, s(br), $-NH_2$), 6.61–7.33 (6H, m, aromatic) ppm.

### 2.2.5. 1,2-Bis(4-t-butyl-2-isocyanobenzylthio)ethane (L) [13]

A mixture of 4 (0.180 g, 0.43 mmol), sodium hydroxide (0.500 g), chloroform (1.3 ml), benzyltriethylammonium chloride (0.130 g) and dichloromethane (7.0 ml) was stirred vigorously overnight at room temperature under nitrogen atmosphere. After addition of water (20 ml), the reaction mixture was extracted three times with dichloromethane (50 ml). Dichloromethane was removed under vacuum, and the concentrate was applied to the top of a chromatography column ($150 \times 25$ mm) of silica gel (60–80 mesh, Kanto Chemical) and eluted with benzene. The second fraction was evaporated under diminished pressure to give a highly viscous yellow oil; yield 0.047 g (25%). After being allowed to stand for a week in a refrigerator (5 °C), the oily product solidified. IR data (KBr disk) $cm^{-1}$: 2955, 2860 (C–H str., s), 2100 (N≡C str., s), 660 (C–S str., m). EI-MS: $m/z$ (relative intensity) 436 (12.0, $M^+$), 265 (5.61, $[M+1-(C_{12}H_{14}N)]^+$), 264 (20.6, $[M-(C_{12}H_{14}N)]^+$), 173 (28.4, $[M+1-(C_{14}H_{18}NS_2)]^+$), 172 (100, $[M-(C_{14}H_{18}NS_2)]^+$) (molecular weight 436.68). $^1H$ NMR (chloroform-$d_1$, TMS): $\delta$ 1.29 (18H, s, $(CH_3)_3C-$), 2.57 (4H, s, $-SCH_2-CH_2S-$), 3.64 (4H, s, Ar–$CH_2S-$), 6.53–7.53 (6H, m, aromatic) ppm. Anal. Calc. for $C_{26}H_{32}N_2S_2$: C, 71.51; H, 7.39; N, 6.42. Found: C, 71.65; H, 7.41; N, 6.53%.

### 2.3. Preparation of the diisonitrile complexes

#### 2.3.1. Bis(1,2-bis(4-t-butyl-2-isocyanobenzylthio)-ethane)rhodium(I) chloride (RhL₂Cl)

A mixture of L (0.170 g, 0.390 mmol), bis($\eta$-1,5-cyclooctadiene)-$\mu,\mu'$-dichlorodirhodium(I) [14] (0.050

g, 0.100 m mol) and benzene (5.0 ml) was stirred for 3 h at room temperature under nitrogen atmosphere. Hexane (10 ml) was added until a slight turbidity developed. After the mixture was permitted to stand overnight in a refrigerator, the product was separated by filtration and washed three times with diethyl ether (10 ml) to give a brown microcrystalline solid; yield 0.070 g (35.5%), m.p. 169–180 °C (dec.). Anal. Calc. for $C_{52}H_{64}N_4S_4RhCl$: C, 61.73; H, 6.38; N, 5.54. Found: C, 61.88; H, 6.49; N, 5.50%.

#### 2.3.2. Bis(1,2-bis(4-t-butyl-2-isocyanobenzylthio)-ethane)rhodium(I) tetrafluoroborate (RhL₂BF₄)

A mixture of $RhL_2Cl$ (0.070 g, 0.069 mmol), sodium tetrafluoroborate (0.012 g, 0.104 mmol) and dichloromethane (10 ml) was stirred for 3 h at room temperature under nitrogen atmosphere. The insoluble material was filtered out and to the filtrate was added hexane (50 ml) until the crystalline product was deposited. The product was collected by filtration and washed three times with diethyl ether (20 ml) to give a brown microcrystalline solid; yield 0.035 g (47.6%), m.p. 180–190 °C (dec.). Anal. Calc. for $C_{52}H_{64}N_4S_4RhBF_4$: C, 58.75; H, 6.07; N, 5.27. Found: C, 58.83; H, 5.87; N, 5.08%.

#### 2.3.3. Bis(1,2-bis(4-t-butyl-2-isocyanobenzylthio)-ethane)copper(I) tetrafluoroborate (CuL₂BF₄)

A mixture of tetrakis(acetonitrile)copper(I) tetrafluoroborate [15] (0.48 g, 1.49 mmol), L (0.670 g, 1.54 mmol) and benzene (5.0 ml) was stirred for 5 h at room temperature under nitrogen atmosphere. Diethyl ether (20 ml) was added to the reaction mixture until a finely dispersed precipitate was observed. After the mixture was allowed to stand overnight in a freezer, the product was removed by filtration and washed three times with diethyl ether (20 ml) to give a yellow microcrystalline solid; yield 0.170 g (21.6%), m.p. 165.0–171.1 °C (dec.). Anal. Calc. for $C_{52}H_{64}N_4S_4CuBF_4$: C, 61.01; H, 6.30; N, 5.47. Found: C, 61.18; H, 6.38; N, 5.44%.

#### 2.3.4. Dichloro(1,2-bis(4-t-butyl-2-isocyanobenzylthio)-ethane)palladium(II) (PdLCl₂)

A mixture of palladium(II) chloride (0.200 g, 1.127 mmol), L (1.01 g, 2.317 mmol) and acetonitrile (20.0 ml) was kept under reflux with stirring for 6 h. After the mixture was allowed to stand at room temperature for 8 h, the crystalline product was removed from the reaction mixture by filtration and washed three times with diethyl ether (20 ml) to give a dark brown microcrystalline solid; yield 0.243 g (35.1%), m.p. 230.4–231.7 °C (dec.). Anal. Calc. for $C_{26}H_{32}Cl_2N_2S_2Pd$: C, 50.86; H, 5.25; N, 4.56. Found: C, 50.58; H, 5.66; N, 4.27%.

## 3. Results and discussion

### 3.1. Synthesis of the diisonitrile ligand

The diisonitrile ligand was synthesized as shown in Scheme 2, with a maximum overall yield of 7.3%. The first step in this scheme utilizes chloromethylation to give the chloromethylated compound (1). The second step employs the nitrating reaction to yield the nitro species (2). The third step uses the condensation of 2 and 1,2-ethanedithiol with base to produce the dinitro compound (3). Reduction of the nitro group of 3 leads to the diamino species (4). The diisonitrile ligand L is prepared in 25% yield by the carbylamine reaction, under vigorous stirring, of a mixture of aqueous sodium hydroxide, chloroform, 4 and benzyltriethylammonium chloride in dichloromethane at room temperature. The product is an air-stable (for over a year), highly viscous yellow oil and coagulates after being permitted to stand for a week in a refrigerator. It has been fully characterized by elemental analysis and infrared and $^1$H NMR spectroscopy (data given in Tables in this paper). L is extremely soluble in chloroform and dichloromethane; even in diethyl ether it is soluble, while in hexane it is only slightly soluble. Compared with many other isonitrile ligands, L is easy to study owing to its air stability and lack of smell.

### 3.2. Metal complexes of the bidentate diisonitrile ligand

The reaction of palladium(II) chloride with L in acetonitrile under refluxing for 6 h leads to PdLCl$_2$ in 35.1% yield. On the other hand, the reaction of Cu(CH$_3$CN)$_4$BF$_4$ with L takes place at room temperature for 5 h to give CuL$_2$BF$_4$ in 21.6% yield. In a somewhat slower reaction at room temperature, bis($\eta$-1,5-cyclooctadiene)-$\mu,\mu'$-dichlorodirhodium(I) reacts with L to afford RhL$_2$Cl in 35.5% yield. RhL$_2$BF$_4$ complex is obtained in 47.6% yield by the anion-exchange reaction of RhL$_2$Cl with NaBF$_4$ in dichloromethane. It can be seen that the reactions for the formation of CuL$_2$BF$_4$ and RhL$_2$Cl proceed swiftly at room temperature. The analytical data and melting
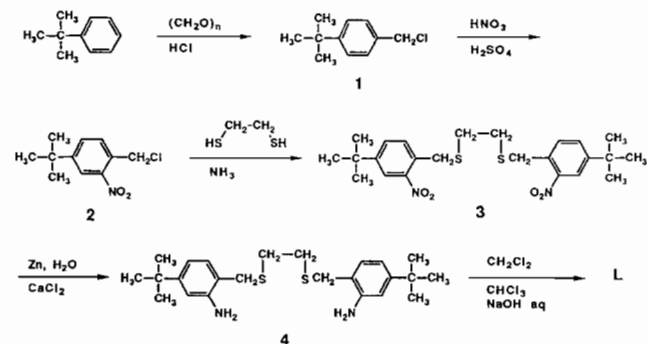
points for these complexes have been given in Section 2. The elemental analyses of RhL$_2$Cl, RhL$_2$BF$_4$, CuL$_2$BF$_4$ and PdLCl$_2$ complexes are consistent with the expected compositions.

### 3.3. Molar conductances

The molar conductances for the complexes are summarized in Table 1. RhL$_2$Cl, RhL$_2$BF$_4$ and CuL$_2$BF$_4$ are 1:1 electrolytes in acetonitrile solutions and tetra-coordinated in this solvent. Therefore, the tetrafluoroborate and chloride anions are ionized upon dissolution in this solvent. The molar conductance of PdLCl$_2$ is nearly equal to zero. Consequently, two chloride anions are not ionized upon dissolution in the solvent.

### 3.4. Mass spectra

The FAB mass spectra, obtained in a glycerin matrix using xenon in the fast atom beam, establish a cluster of ions corresponding to $[M-BF_4+1]^+$ or $[M-Cl]^+$ for RhL$_2$BF$_4$, CuL$_2$BF$_4$ and RhL$_2$Cl complexes. Table 2 lists the molecular weights and the ions observed. Molecular ions were not observed, since the samples were analyzed employing the FD and the EI mass spectra. On the other hand, the PdLCl$_2$ complex shows the presence of a molecular ion $M^+$ at $m/z$ 612 in the EI mode at 20 eV, but the relative intensity is very small. These results are substantiated by the molar conductance results.

Table 1
Molar conductances of the complexes in acetonitrile at $25.0 \pm 0.2$ °C

| Complex | $\Lambda_M$[a] $(\Omega^{-1}$ cm$^2$ mol$^{-1})$ | Type of electrolyte [b] |
|---|---|---|
| RhL$_2$BF$_4$ | 153 | 1:1 |
| RhL$_2$Cl | 129 | 1:1 |
| CuL$_2$BF$_4$ | 132 | 1:1 |
| PdLCl$_2$ | $\approx 0$ | |

[a] For $\sim 10^{-3}$ mol dm$^{-3}$ solutions.
[b] Assignments of the type of electrolyte present in solution were made on the basis of the conductance data compiled by Geary [16].

Table 2
Characteristic ions observed in mass spectra for the complexes

| Complex | Molecular weight | Ion observed [a] |
|---|---|---|
| RhL$_2$BF$_4$ | 976 | $[M-BF_4+1]^+$ |
| RhL$_2$Cl | 975 | $[M-Cl]^+$ |
| CuL$_2$BF$_4$ | 936 | $[M-BF_4+1]^+$ |
| PdLCl$_2$ | 612 | $[M]^+$ |

[a] $M$ is a molecular ion.



Scheme 2. Synthesis of the diisonitrile ligand L.

## 3.5. Vibrational spectra

The characteristic IR bands that are meaningful for the present discussion are listed in Table 3. The diisonitrile ligand (L) exhibits a strong band at 2100 $cm^{-1}$, which is correlated with a $N \equiv C$ stretching mode [7,17]. This band shows a large shift (by 50–100 $cm^{-1}$) to higher frequency upon metal coordination, because of the inductive effect caused by the positive charge of the metal ions. The magnitude of the shift is approximately proportional to that of the increasing positive charge on the complex. This spectral action is comparable to that observed for the diisonitrile com-

Table 3
Characteristic IR bands for the diisonitrile ligand L and its complexes [a]

| Compound | IR bands [b] ($cm^{-1}$) | |
| --- | --- | --- |
| | $\nu(N \equiv C)$ | $\nu(B-F)$ |
| L | 2100(s) | |
| $RhL_2BF_4$ | 2170(s) | 1045(s,br) |
| $RhL_2Cl$ | 2170(m) | |
| $CuL_2BF_4$ | 2150(s) | 1050(s,br) |
| $PdLCl_2$ | 2200(m) | |

[a] In a KBr pellet.
[b] Relative intensities: s, strong; m, medium; br, broad.

Table 4
Proton NMR data for the diisonitrile ligand and its complexes [a]

| Compound | Aromatic Ar–$H$ | Methylene | | t-Butyl –$CH_3$ |
| --- | --- | --- | --- | --- |
| | | Ar–$CH_2$– | –$CH_2$– | |
| L [b] | 6.53–7.53(m) | 2.57(s) | 3.64(s) | 1.29(s) |
| $RhL_2BF_4$ [b] | 7.23–8.19(m) | 2.59(s) | 3.83(s) | 1.32(s) |
| $RhL_2Cl$ [c] | 7.25–8.37(m) | 2.58(s) | 3.79(s) | 1.30(s) |
| $CuL_2BF_4$ [b] | 7.12–8.06(m) | 2.58(s) | 3.65(s) | 1.26(s) |
| $PdLCl_2$ [b] | 7.37–8.50(m) | 3.42(s) | 4.45(s) | 1.32(s) |

[a] Chemical shifts are given in ppm from internal TMS. The multiplicity of a proton signal is given in parentheses after the $\delta$ value: s, singlet; m, multiplet.
[b] Measured in chloroform-$d_1$.
[c] Measured in dimethyl sulfoxide-$d_6$.

plexes reported by Angelici et al. [6,7]. Consequently, this suggests that L serves primarily as a $\sigma$-donor. A strong, broad absorption band at about 1050 $cm^{-1}$ was observed for all of the tetrafluoroborate complexes and is attributable to the B–F stretching mode [18]. Since no shift of the band was detected, the tetrafluoroborate group in the present complexes is present not as a coordinated group but as a simple isolated ion [19]. This result is supported by the molar conductances and the mass spectral data.

## 3.6. NMR spectra

The proton NMR signals and their assignments for the diisonitrile ligand and its complexes are compiled in Table 4. The methylene protons of the benzyl group and the bridging group for L, $RhL_2BF_4$, $RhL_2Cl$, $CuL_2BF_4$ and $PdLCl_2$ do not couple with any protons, the methylene signal being a singlet. The methyl signal of the t-butyl group is also a singlet, because there is no coupling with any protons. On the other hand, the aromatic protons couple with each other and the signals are a multiplet. The methylene proton signals of the benzyl group and the bridging group are shifted slightly downfield upon the formation of $RhL_2BF_4$, $RhL_2Cl$ and $CuL_2BF_4$ complexes. The chemical shifts of the methylene proton in the $PdLCl_2$ complex are all at lower field than those in $RhL_2BF_4$, $RhL_2Cl$ and $CuL_2BF_4$ complexes. This downfield shift is associated with the deshielding effect due to the positive charge provided by the metal ion in the complexes. Since the oxidation number of the palladium atom is greater than that of the copper and rhodium atoms, the deshielding effect for the $PdLCl_2$ complex is much greater than that for the $RhL_2BF_4$, $RhL_2Cl$ and $CuL_2BF_4$ complexes. Furthermore, the magnitude of the shift for the bridging group is larger than that for the benzyl group. This seems to indicate that the monovalent and divalent metal complexes could be distinguished by the proton NMR signals of the methylene group in the complexes, because it is proportional to the magnitude of the oxidation number. The other proton signals are shifted downfield slightly upon metal coordination. Since the

Table 5
Electronic absorption bands for the diisonitrile ligand and its complexes

| Compound | Transition energy in nm ($\epsilon$) [a] | |
| --- | --- | --- |
| | $\pi \to \pi^*$/CT | $d \to d^*$ |
| L | 289(10400) | |
| $RhL_2BF_4$ | 248sh(19300), 290sh(12000) | 360sh(9780), 420sh(3050), 471(1600) |
| $RhL_2Cl$ | 245sh(19100), 289sh(11800) | 357sh(9800), 422sh(3100), 470(1650) |
| $CuL_2BF_4$ | 246sh(17900), 292sh(11500) | |
| $PdLCl_2$ | 249sh(16500), 298(12100) | 360sh(6500), 430(2600) |

[a] Measured in methanol at room temperature; sh indicates a shoulder band.

results are analogous to those for the diisonitrile complexes [6,7], the ligand in these complexes acts not as a $\pi$-acceptor but as a $\sigma$-donor. It is surprising that the diisonitrile ligand L does not coordinate through the thioethereal sulfur atoms in the bridging group rather than the isonitriles, because the S-coordinated form would have a stable five-membered-ring structure and the isonitrile coordination makes a fifteen-membered-ring structure.

## 3.7. Electronic spectra

Table 5 presents electronic absorption data for the diisonitrile ligand and its complexes. The spectra of these compounds are similar to those of the diisonitrile complexes reported by Angelici et al. [3,6]. On the basis of the assignments made by Angelici et al. for diisonitrile complexes [3,6], the absorption bands are attributed to $\pi \rightarrow \pi^*$ transitions within the ligand and/ or charge transfer (CT) transitions from metal to ligand in the 245–298 nm region, and to $d \rightarrow d^*$ transitions in the 357–471 nm range.

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