Inorganica Chimica Acta, *84* (1984) 89–94

Synthesis of some Novel Pt(II) and Pd(II) N-alkyliminodithiocarbonato Complexes and Investigation of the Mechanism of their Formation by CNDO/2 Quantum Chemical Calculations

G. A. KATSOULOS and C. A. TSIPIS*

Laboratory of Inorganic Chemistry, University of Thessaloniki, Thessaloniki, Greece

Received July 18, 1983

A new series of bis(phosphine)(N–alkyliminodithiocarbonato)platinum(II) and palladium(II) complexes has been synthesised and studied. The spectroscopic and magnetic data of the new compounds are in accordance with a square-planar configuration with C_{2v} local symmetry. A possible mechanism has also been proposed for the formation of the complexes with respect to the results of quantum chemical CNDO/2 calculations. On the basis of these results the different behaviour of the coordinated uni- and bidentate N–alkyldithiocarbamato ligands against nucleophiles was established and their deprotonation and protonation reactions were explained.

Introduction

It is well established [1–6] that the reaction of all $[M(S–S)_2]$ complexes $[M = Pt$ or Pd; $(S–S)^- = R_2NCS_2^-$, $ROCS_2^-$, $(RO)_2PS_2^-$ and $R_2PS_2^-]$ with tertiary phosphines occurs by stepwise cleavage of metal–sulphur bonds to generate the four-coordinate square-planar $[M(S–S)_2(PR'_3)]$ and $[M(S–S)(PR'_3)_2]^+(S–S)^-$ complexes which exhibit unidentate/bidentate and bidentate/ionic modes of bonding of the dithioacid groups respectively. Furthermore, reacting the xanthate and dithiophosphate complexes with excess tertiary phosphine [3, 5] nucleophilic attack by $(S–S)^-$ on a coordinated alkoxy-group can occur to give the compounds $[M(S_2CO)(PR'_3)_2]$ and $[M\{S_2P(O)OR\}(PR'_3)_2]$ respectively.

Considering the above results we extended the study of the aforesaid reactions to the corresponding bis(N–monosubstituted-dithiocarbamato) complexes, since N–alkyldithiocarbamato ligands are isoelectronic to the xanthate ligands. In a previous communication [7] we have reported some preliminary results concerning the reactions of bis(N–alkyldithiocarbamato)platinum(II) complexes with tricyclohexylphosphine and γ-picoline. In view of these results it was of interest to extend the study of this type of reaction in order to find out whether the behaviour of the $\{RHNCS_2\}^-$ ligands is similar to that of the isoelectronic xanthate ligands with respect to the formation of $[M(S_2C{=}NR)(PR'_3)_2]$ complexes.

In the present paper we report on our results concerning the synthesis and characterization of novel bis(phosphine)(N–alkyliminodithiocarbonato)platinum(II) and palladium(II) complexes. In an attempt to understand the mechanism of the formation of these complexes, the results of quantum chemical CNDO/2 calculations on the ligands have been also included.

Experimental

Physical Measurements

Infrared spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets or Nujol mulls. ^{1}H NMR spectra were recorded on a Varian A 60A (60 Mc/s) instrument in $CDCl_3$ solutions using TMS as an internal standard. Electronic spectra were obtained with a Cary 17DX spectrophotometer using freshly prepared $CHCl_3$ solutions. Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with ionisation source of T-2p type operating at 70 eV. Molecular weights were determined using a Perkin-Elmer molecular weight apparatus Model 115 in $CHCl_3$ solutions. The determination of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240 Elemental

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*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. Analytical Data[a], Melting Points (°C), Molecular Weights, and Relevant IR Frequencies (cm^{-1}) of the New N–alkyliminodithiocarbonato Complexes[b] of Pt(II) and Pd(II) with their Assignments (KBr discs).[c]

Compound	M.P.	%C	%N	%H	%M[d]	M.W.	ν(C=N)	ν(C–S)	ν(M–S)
$[Pt(S_2C{=}NBz)(PMe_2Ph)_2]$	176–178	43.78	1.98	4.43	31.05	638	1579vs	903s	368m
		(44.17)	(2.15)	(4.48)	(29.89)	(652.7)			285w
$[Pt(S_2C{=}NBz)(diphos)]$	233–235	51.82	2.05	4.16	24.65	765	1582vs	885m	370m
		(52.71)	(1.81)	(4.03)	(25.18)	(774.8)			288w
$[Pt(S_2C{=}NBu^t)(PMe_2Ph)_2]$	152–154	41.25	2.30	5.25	32.10	630	1580vs	905s	370m
		(40.77)	(2.26)	(5.05)	(31.53)	(618.6)			288w
$[Pt(S_2C{=}NBu^t)(diphos)]$	209–211	50.18	1.71	4.61	26.55	750	1587vs	892s	368m
		(50.26)	(1.89)	(4.49)	(26.34)	(740.8)			282w
$[Pd(S_2C{=}NBz)(PMe_2Ph)_2]$	141–143	51.74	2.61	5.14	18.93	535	1562vs	900s	342m
		(51.11)	(2.48)	(5.18)	(18.87)	(564.0)			275w
$[Pd(S_2C{=}NBz)(diphos)]$	177–179	58.82	2.02	4.80	15.30	660	1564vs	880m	340m
		(59.52)	(2.04)	(4.55)	(15.51)	(686.1)			277w
$[Pd(S_2C{=}NBu^t)(PMe_2Ph)_2]$	127–129	48.10	2.66	6.13	20.37	505	1562vs	903s	345m
		(47.59)	(2.64)	(5.90)	(20.08)	(530.0)			275w
$[Pd(S_2C{=}NBu^t)(diphos)]$	135–137	57.65	2.19	5.31	15.84	680	1565vs	890s	340m
		(57.10)	(2.15)	(5.10)	(16.32)	(652.1)			280w

[a] Figures in parentheses are the calculated values. [b] Abbreviations used throughout: Bz = benzyl, Me = methyl, Ph = phenyl, diphos = 1,2-bis(diphenylphosphine)ethane, Bu^t = tert-butyl. [c] vs = very strong, s = strong, m = medium, w = weak. [d] M = Pt or Pd.

Analyser. Platinum and palladium were determined according to published methods [8].

MO Calculations

All MO calculations were performed using the SCF-LCAO-MO method within the CNDO/2 approximation [9]. Bond lengths and valence angles were obtained from X-ray structures of the complexes [10, 11] and in some cases using standard geometries.

Preparation of the Complexes

The bis(N–benzyldithiocarbamato)platinum(II), $[Pt(S_2CNHBz)_2]$, was prepared as described previously [7]. A similar method was also employed for the preparation of the corresponding palladium(II) complex, $[Pd(S_2CNHBz)_2]$. The bis(N–*t*-butyldithiocarbamato)platinum(II), $[Pt(S_2CNHBu^t)_2]$, and bis(N–*t*-butyldithiocarbamato)palladium(II), $[Pd(S_2CNHBu^t)_2]$, were also prepared as described elsewhere [12].

Bis(dimethylphenylphosphine)(N–alkyliminodithiocarbonato)platinum(II) and palladium(II) complexes

A suspension of 1 mmol of the appropriate bis(N–alkyldithiocarbamato)platinum(II) or palladium(II) complex in 10 ml of toluene was treated with 0.22 ml (2 mmol) of dimethylphenylphosphine and the mixture was left at room temperature under continuous magnetic stirring. After a period of 12 h. a white precipitate was formed and the precipitation was completed by addition of 20 ml of light petroleum (b.p. 50–60 °C). The white precipitate was filtered off, washed with diethyl ether and dried under vacuum. Recrystallisation of the complexes was carried out from acetone.

[1,2-bis(diphenylphosphine)ethane](N–alkyliminodithiocarbonato)platinum(II) and palladium(II) complexes

1 mmol of the appropriate bis(N–alkyldithiocarbamato)platinum(II) or palladium(II) complex was suspended in 10 ml of toluene and treated with 0.39 g (1 mmol) of 1,2-bis(diphenylphosphine)ethane (diphos) dissolved in 5 ml of toluene. The resulting clear solution was left at room temperature under continuous magnetic stirring. After a period of 0.5 h. a white precipitate was formed and the precipitation was completed by addition of 30 ml of light petroleum (b.p. 50–60 °C). The white precipitate was filtered off, washed with diethyl ether, and dried under vacuum. Recrystallisation was carried out from acetone.

Results and Discussion

The reaction of bis(N–alkyldithiocarbamato)platinum(II) or palladium(II) complexes, $[M(S_2CNHR)_2]$ (R = benzyl or *t*-butyl), with dimethylphenylphosphine, PMe_2Ph, (1:2 molar ratio) or 1,2-bis(diphenylphosphine)ethane, $Ph_2PCH_2CH_2PPh_2$, (1:1 molar ratio) readily gives white solid compounds of stoichiometry $[M(S_2C{=}NR)(PMe_2Ph)_2]$ and $[M(S_2$-

C=NR)(diphos)] respectively. These new N–alkyliminodithiocarbonato complexes (dithiocarbimate complexes) are some of the few examples in the pure chemistry of the N–alkyliminodithiocarbonato ligands. Until recently only complexes of the $\{(CN)\text{-}N{=}CS_2\}^{2-}$ ligand and the bis-nickel complex of the $\{PhN{=}CS_2\}^{2-}$ ligand had been reported [13]. The formation of N–alkyliminodithiocarbonato complexes of the general formula [$L_2M(S_2C{=}NR)$] [L = PPh_3, R = Ph or Me and M = Pt(II)] by the reaction of coordinated organic isothiocyanates with excess isothiocyanates had also been reported [14].

TABLE II. ^{1}H NMR Chemical Shifts (τ ppm) of the New N–alkyliminodithiocarbonato Complexes of Pt(II) and Pd(II) in Chloroform-d.

Compound	Chemical Shifts
[Pt($S_2C{=}NBz$)(PMe_2Ph)$_2$]	8.42(t of d, 12H, P–CH_3, $^2J_{P\text{–}H}$ = 11 Hz, $^3J_{^{195}Pt\text{–}H}$ = 32 Hz)[a]; 5.13(s, 2H, N–CH_2); 2.63(m, 15H, C_6H_5)
[Pt($S_2C{=}NBz$)(diphos)]	7.54(mu, 4H, P–CH_2); 5.21(s, 2H, N–CH_2); 2.68(m, 25H, C_6H_5)
[Pt($S_2C{=}NBu^t$)(PMe_2Ph)$_2$]	8.43(t of d, 12H, P–CH_3, $^2J_{P\text{–}H}$ = 11 Hz, $^3J_{^{195}Pt\text{–}H}$ = 32 Hz); 7.59(s, 9H, C–CH_3); 2.67(m, 10H, C_6H_5)
[Pt($S_2C{=}NBu^t$)(diphos)]	8.10(s, 9H, C–CH_3); 7.52(mu, 4H, P–CH_2); 2.34(m, 20H, C_6H_5)
[Pd($S_2C{=}NBz$)(PMe_2Ph)$_2$]	8.40(m, 12H, P–CH_3, $^2J_{P\text{–}H}$ = 10.5 Hz); 5.15(s, 2H, N–CH_2); 2.62(m, 15H, C_6H_5)
[Pd($S_2C{=}NBz$)(diphos)]	7.56(mu, 4H, P–CH_2); 5.22(s, 2H, N–CH_2); 2.65(m, 25H, C_6H_5)
[Pd($S_2C{=}NBu^t$)(PMe_2Ph)$_2$]	8.45(m, 12H, P–CH_3, $^2J_{P\text{–}H}$ = 10.5 Hz); 7.75(s, 9H, C–CH_3); 2.66(m, 10H, C_6H_5)
[Pd($S_2C{=}NBu^t$)(diphos)]	8.20(s, 9H, C–CH_3); 7.56(mu, 4H, P–CH_2); 2.35(m, 20H, C_6H_5)

[a] s = singlet, t of d = triplet of doublets, m = multiplet, mu = multiplet unresolved.

The analytical data for the new compounds, their melting points and molecular weights, as well as the most relevant absorption bands in the IR spectra of the studied compounds and their assignments, are shown in Table I. All compounds, which were obtained in 60–70% yields, were white microcrystalline solids, stable in air either in solution or in the solid state. They were soluble in most of the common organic solvents, such as chloroform, acetone, methylene chloride, but were insoluble in ethanol, diethyl ether, carbon tetrachloride and water.

Characterization of the Complexes

The characterization of the novel N–alkyliminodithiocarbonato complexes of Pt(II) and Pd(II) was established by spectroscopic methods (IR, ^{1}H NMR, UV–Vis, and MS), magnetic measurements and the results of protonation reactions.

All the compounds show a very strong absorption band in the 1560–1580 cm^{-1} region. This band is attributed to the stretching vibration of the C=N bond of the N–alkyliminodithiocarbonato ligand. The position of the band is affected by the nature of the central atom and is shifted to lower frequencies in the Pd(II) complexes. This is a reflection of the higher electron acceptor ability of Pt(II) than Pd(II). By protonation of the complexes with trifluoroacetic acid the ν(C=N) band is shifted to lower frequencies and its position is the same with the $\nu(C\overset{\cdot\cdot}{-}N)$ band of the corresponding N–alkyldithiocarbamato complexes of Pt(II) and Pd(II) [7, 12]. Furthermore, a new broad band in the 3300 cm^{-1} region appeared, which is also characteristic of the N–alkyldithiocarbamato complexes. The band in the region of 880–905 cm^{-1} is attributed to the stretching vibration of the C–S bonds. This band is shifted to lower frequencies relative to the ν(C–S) band of the corresponding N–alkyldithiocarbamato ligands [7, 12]. This is expected since the C–S bonds in the N–alkyldithiocarbamato ligands show a partial double bond character, as it results from CNDO/2 calculations as well as from X-ray structure determination [10]. Finally, the M–S stretching frequencies were observed in the 270–370 cm^{-1} region indicating the coordination of the gem-disulfide ligand.

TABLE III. Electronic Spectra of the New N–alkyliminodithiocarbonato Complexes of Pt(II) and Pd(II) in $CHCl_3$.

Compound	Band I	Band II	Band III	Band IV	Band V	Band VI
$[Pt(S_2C{=}NBz)(PMe_2Ph)_2]$	41.7^a(4.68)^b	37.7 (4.53)	34.1sh^c(4.20)	31.9 (3.55)	29.7 (2.98)	16.2 (1.68)
$[Pt(S_2C{=}NBz)(diphos)]$	41.6 (4.72)	37.5 (4.59)	34.1sh (4.18)	31.7 (3.71)	29.8 (3.00)	16.3 (1.68)
$[Pt(S_2C{=}NBu^t)((PMe_2Ph)_2]$	41.7 (4.55)	37.5 (4.60)	34.5sh (4.05)	31.9 (3.42)	29.8 (3.07)	16.5 (1.65)
$[Pt(S_2C{=}NBu^t)(diphos)]$	41.7 (4.61)	37.6 (4.55)	34.3sh (4.11)	32.3 (3.20)	29.9 (2.98)	16.5 (1.69)
$[Pd(S_2C{=}NBz)(PMe_2Ph)_2]$	40.9 (4.80)	37.5 (4.73)	33.2sh (4.28)	31.1 (4.32)	28.5 (3.54)	16.3 (1.75)
$[Pd(S_2C{=}NBz)(diphos)]$	40.9 (4.82)	37.2 (4.76)	33.1sh (4.25)	31.1 (4.31)	28.3 (3.62)	16.1 (1.72)
$[Pd(S_2C{=}NBu^t)(PMe_2Ph)_2]$	41.2 (4.69)	37.1 (4.80)	33.7sh (4.28)	31.4 (4.25)	28.5 (3.68)	16.6 (1.76)
$[Pd(S_2C{=}NBu^t)(diphos)]$	41.1 (4.72)	37.3 (4.76)	33.6sh (4.23)	31.5 (4.32)	28.7 (3.71)	16.6 (1.77)

$^a\nu$/kK; $^b\log \epsilon_{mol}$; ^{c}sh = shoulder.

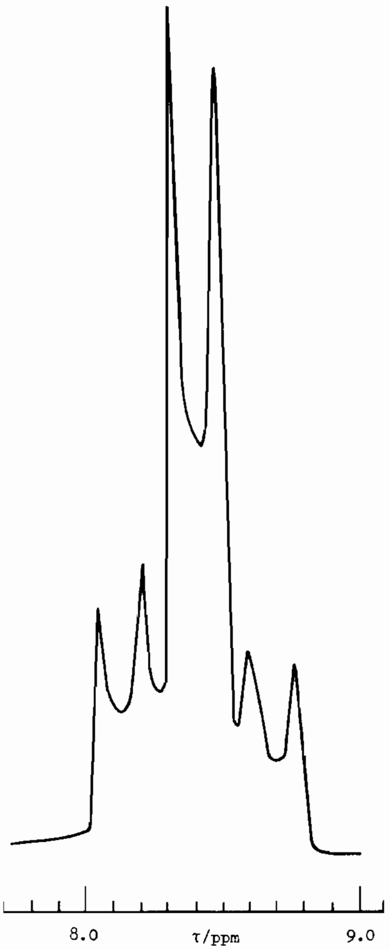


Fig. 1. ^1H NMR spectrum of $[Pt(S_2C{=}NBz)(PMe_2Ph)_2]$ at 37 °C, 60 MHz in $CDCl_3$: methyl region.

The IR data, the diamagnetic nature of the complexes under investigation and their stoichiometry allowed us to suggest a square-planar configuration with local symmetry belonging to C_{2v} point group. This structure is further supported from the ^1H NMR spectra of the complexes.

The signals of the ^1H NMR spectra of the new compounds are reported in Table II. The phosphine methyl proton signal of $[Pt(S_2C{=}NR)(PMe_2Ph)_2]$ complexes appears as a triplet (1:4:1) of doublets (1:1) six-line pattern (the two outer satellites are due to $^3J_{^{195}Pt-P-C-H}$, $I = ½$, natural abundance 33%). This pattern which is shown in Fig. 1 confirms the direct coordination of the phosphine ligands to the platinum metal center.

The electronic spectra of the new N–alkyliminodithiocarbonato complexes of Pt(II) and Pd(II) are also consistent with the proposed square-planar configuration. The absorption maxima and the extinction coefficients of the bands observed in the electronic spectra of the compounds under investigation are shown in Table III. The most intense band I is due to an intraligand $\pi^* \leftarrow \pi$ transition located on the N=C–S group [15, 16]. This band shows an hypsochromic shift relative to the corresponding band of the N–alkyldithiocarbamato ligand, due to the localisation of the π-electron system in the N–alkyliminodithiocarbonato ligand. Band II is also due to an intraligand $\pi^* \leftarrow \pi$ transition located on the phosphine ligands. Band III, which appears as a shoulder, is attributed to a $\pi^* \leftarrow n$ transition located on the sulfur atoms [17]. Bands IV and V are due to charge transfer (CT) transitions of the types L → M and M → L respectively. These bands are analogous to the CT bands observed in the square-planar complexes of D_{2h} symmetry and are assigned to $^1B_{2u}$, $^1B_{3u} \leftarrow {}^1A_g$ and $^1B_{1u}$, $^1B_{2u}$, $^1B_{3u} \leftarrow {}^1A_g$ transitions, respectively [18]. Finally, band VI can be assigned as a crystal field band on the basis of its low intensity.

The characteristic features of the mass spectra of these compounds are the absence of the peak due to the molecular ion of the complexes and the existence

TABLE IV. The Composition (%) and the Eigenvalues (in a.u.) of the Frontier Orbitals of some Dithio-ligands.

Ligand	MO-type	Eigenvalue	Eigenvectors				
			%SS	%C	%N	%Bu^t	%H
$\{Bu^tNHCSS\}^-$	n-HOMO	−0.1110	85.3	5.3	1.4	6.9	1.1
(unidentate)	π*-LUMO	0.3102	54.2	20.7	11.0	13.7	0.4
$\{Bu^tNHCSS\}^-$	σ-HOMO	−0.1060	79.3	7.4	1.1	10.1	2.1
(bidentate)	σ*-LUMO	0.2235	9.6	3.3	9.8	74.7	2.6
$\{Bu^tN{=}CSS\}^{2-}$	σ-HOMO	0.0962	63.4	9.6	8.2	18.8	–
(bidentate)	σ*-LUMO	0.4150	12.0	3.8	7.7	76.5	–
$\{H_2NCSS\}^-$	n-HOMO	0.0985	99.1	0.6	0.3	–	–
(bidentate)	π*-LUMO	0.3055	67.1	23.1	9.8	–	–
$\{HN{=}CSS\}^{2-}$	σ-HOMO	0.1481	64.8	12.9	16.6	–	5.7
(bidentate)	π*-LUMO	0.6343	66.9	19.9	12.7	–	0.5

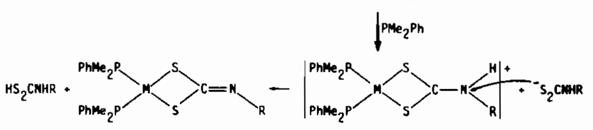
of the peak due to the N–alkyliminodithiocarbonato ligand. The peaks corresponding to higher m/e values can be regarded as direct fragments of the molecular ions, while those at lower m/e values may be regarded as daughter fragments of the phosphine and N–alkyliminodithiocarbonato ligands. In the case of the dimethylphenylphosphine complexes peaks due to the ion $SPMe_2Ph^{+\bullet}$ and its fragments were also observed. In the case of the $[Pd(S_2C{=}NBu^t)(PMe_2Ph)_2]$ complex the existence of a metastable peak at m* = 75.3 confirms the following fragmentation:

$$\overset{+}{P}\dot{d}(S_2C{=}NBu^t) \xrightarrow[*]{-Bu^tN{=}C{=}S\cdot} PdS^{+\bullet}$$

m/e 253 m/e 138

Mechanism of the Formation of the Complexes

In order to gain an insight on the mechanism of the formation of the novel N–alkyliminodithiocarbonato complexes of Pt(II) and Pd(II) both experimental and theoretical results have been used. Stephenson *et al.* [5] suggested for the reaction of platinum (or palladium) xanthates with PR_3 a mechanism which involves a stepwise cleavage of metal–sulfur bonds to give the ionic 1:2 complex, followed by nucleophilic attack of the xanthate anion on the alkoxy-group of the coordinated xanthate ligand to give the neutral dithiocarbonato complex and a xanthate ester. A similar scheme would also explain the formation of the N-alkyliminodithiocarbonato complexes as shown below:



In the first step of the reaction four-coordinate square-planar complexes containing unidentate and bidentate N–alkyldithiocarbamato ligands are formed. These complexes were isolated and their structures were established on the basis of spectroscopic and X-ray crystal structure determination methods [7, 10, 12]. The second step involves the nucleophilic substitution of the unidentate N–alkyldithiocarbamato ligand by the phosphine nucleophile, followed by the nucleophilic attack of the N–alkyldithiocarbamato anion on the coordinated bidentate N–alkyldithiocarbamato ligand. It is evident that the electrophilic centers on the two kinds of N–alkyldithiocarbamato ligands (uni- and bidentate) might be different, considering their different behaviour during the substitution reactions. Therefore, in view of the fact that the nucleophilic substitution reactions take place through HOMO–LUMO interactions, we have justified the different behaviour of the two kinds of N–alkyldithiocarbamato ligands by CNDO/2 calculations of the form of their LUMO. The results are shown in Table IV.

In the unidentate N–alkyldithiocarbamato ligand the LUMO is a π*-MO located on the NCS_2 group and consequently the electrophilic center on this ligand will be located on the NCS_2 group as well. Hence the nucleophilic attack by the phosphine ligand has as a result the substitution of the unidentate N–alkyldithiocarbamato ligand. On the other hand, in the bidentate N–alkyldithiocarbamato ligand the LUMO is a σ*-MO located on the NHR group and consequently the electrophilic center will be also located on this group. Thus, its nucleophilic attack by the N–alkyldithiocarbamato nucleophile will lead to the weakening of the N–H bond and the deprotonation of the ligand. Finally, the above theoretical results also account for the easy substitution of the unidentate N–alkyldithiocarbamato ligand by the nucleophile I^- and the formation of the corresponding iodo-complexes [7, 12].

In Table IV are also included the eigenvectors for the HOMO and LUMO of the $\{H_2NCS_2\}^-$ ligand, as well as of the corresponding iminodithiocarbonato ligand. The form of the LUMO in the case of the $\{H_2NCS_2\}^-$ ligand explains also its inability to undergo deprotonation reactions. On the other hand, the forms of the HOMO of the iminodithiocarbonato ligands explain their electrophilic reactions by the electrophile H^+ which lead to the protonation of the ligands [14].

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