Inorg. Chem. **2003**, *42*, 4268–4274

Inorganic Chemistry
Article

1,1-Ethylenedithiolato Complexes of Palladium(II) and Platinum(II) with Isocyanide and Carbene Ligands

José Vicente,*,[†] María Teresa Chicote, and Sonia Huertas

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Peter G. Jones[‡]

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

Received April 8, 2003

The reactions of $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]_n$ with $[MCl_2(NCPh)_2]$ and CNR (1:1:2) give complexes $[M\{\eta^2\text{-}S_2C{=}C\{C(O)Me\}_2\}(CNR)_2]$ [R = ^{t}Bu, M = Pd (**1a**), Pt (**1b**); R = $C_6H_3Me_2$-2,6 (Xy), M = Pd (**2a**), Pt (**2b**)]. Compound **1b** reacts with $AgClO_4$ (1:1) to give $[\{Pt(CN^tBu)_2\}_2Ag_2\{\mu^2,\eta^2\text{-}(S,S')\text{-}\{S_2C{=}C\{C(O)Me\}_2\}_2\}](ClO_4)_2$ (**3**). The reactions of **1** or **2** with diethylamine give mixed isocyanide carbene complexes $[M\{\eta^2\text{-}S_2C{=}C\{C(O)Me\}_2\}(CNR)\text{-}\{C(NEt_2)(NHR)\}]$ [R = ^{t}Bu, M = Pd (**4a**), Pt (**4b**); R = Xy, M = Pd (**5a**), Pt (**5b**)] regardless of the molar ratio of the reagents. The same complexes react with an excess of ammonia to give $[M\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C\{C(O)Me\}_2\}\text{-}(CN^tBu)\{C(NH_2)(NH^tBu)\}]$ [M = Pd (**6a**), Pt (**6b**)] or $[M\{\eta^2\text{-}(S,S')\text{-}S_2C{=}C\{C(O)Me\}_2\}\{C(NH_2)(NHXy)\}_2]$ [M = Pd (**7a**), Pt (**7b**)] probably depending on steric factors. The crystal structures of **2b**, **4a**, and **4b** have been determined. Compounds **4a** and **4b** are isostructural. They all display distorted square planar metal environments and chelating planar *E,Z*-2,2-diacetyl-1,1-ethylenedithiolato ligands that coordinate through the sulfur atoms.

Introduction

Although 1,2-ethylenedithiolato metal complexes have been much more intensively studied[1] than their isomers with 1,1-ethylenedithiolato ligands, the latter have recently attracted much attention mainly because of the interesting photophysical properties[2−6] derived from their extensive electronic delocalization (push−pull ethylenes). Most studies focus on their solvatochromic behavior and room-temperature luminescence in solution[7−10] and on their possible application as catalysts in light-to-chemical-energy conversion processes.[11] The 1,1-ethylenedithiolato ligands have also been used to stabilize unusually high oxidation states[12−14] or to facilitate the syntheses of clusters.[15−21] Most 1,1-ethylenedithiolato complexes are mononuclear[7−9,12−14,22−27] although some polynuclear complexes[28−31] including clusters[15,18,19,32−37] are known.

2,2-Diacetyl-1,1-ethylenedithiolato complexes are very scarce and, until very recently, only a few derivatives

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[†] E-mail: jvs@um.es, mch@um.es. www: http://www.um.es/gqo/.
[‡] E-mail: p.jones@tu-bs.de.

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10.1021/ic0343758 CCC: $25.00

containing Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II), were described[38] and only characterized by their elemental analyses. We have described a family of 2,2-diacetyl-1,1-ethylenedithiolato complexes of Tl(I), Au(I), Au(III),[39,40] Pd(II), and Pt(II)[41,42] including mononuclear, heterodinuclear [MM′ (M = Pd, Pt; M′ = Ag, Au)] trinuclear [MM'_2 (M = Pd, Pt, M′ = Ag; M = Pt, M′ = Au; M = Ni, Pt, Cd, Hg, M′ = Pt)] and tetranuclear [$M_2M'_2$ (M = Pd, Pt, M′ = Ag; M = Pt, M′ = Au)] derivatives. Among other 1,1-ethylenedithiolato complexes of platinum(II), Eisenberg has described $[Pt\{S_2C{=}C\{C(O)Me\}_2\}(dbbpy)]$[27] (dbbpy = di-*tert*-butylbipyridine) and shown it to possess solvatochromic and luminescent properties, as do many platinum complexes containing diimine and dithiolato ligands.[25,43−45] We report here Pd(II) and Pt(II) 1,1-ethylenedithiolato complexes that are the first containing isocyanide and carbene ligands.

Experimental Section

Elemental analyses, melting points, molar conductivities in acetone solutions, and infrared, ^1H, and ^{13}C NMR spectra in $CDCl_3$ were obtained as described elsewere.[46] *trans*-$[MCl_2(NCPh)_2]$ (M = Pd, Pt) were prepared by refluxing the corresponding MCl_2 in PhCN for 4 h followed by filtration of the hot solution through anhydrous $MgSO_4$, concentration, and addition of Et_2O.[47] $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]$ was prepared as previously reported.[40] $AgClO_4$ (Aldrich), ^tBuNC, XyNC (Xy = $C_6H_3Me_2$-2,6), $NHEt_2$ (Fluka), and NH_3 (Carburos Metálicos) were obtained from commercial sources and used without further purification.

Caution! Perchlorato complexes are potentially explosive. Preparations on a larger scale than that described here should be avoided.

$[M\{\eta^2-(S,S')-S_2C{=}C\{C(O)Me\}_2\}(CNR)_2]$ [R = ^{t}Bu, M = Pd (1a), Pt (1b); R = Xy, M = Pd (2a), Pt (2b)]. To a suspension of $[Tl_2\{S_2C{=}C\{C(O)Me\}_2\}]_n$ (ca. 0.4 mmol) in CH_2Cl_2 (40 mL) were successively added the equimolar amount of $[MCl_2(NCPh)_2]$ and 2 equiv of the appropriate isocyanide. The reaction mixture was stirred for 3 h and then filtered through Celite. The yellow solution was concentrated (3 mL) and Et_2O (40 mL) added to precipitate a yellow solid, which was recrystallized from CH_2Cl_2 and Et_2O and suction dried.

Compound 1a. Yield: 75%. Anal. Calcd for $C_{16}H_{24}N_2O_2PdS_2$: C, 43.05; H, 5.42; N, 6.28; S, 14.34. Found: C, 42.94; H, 5.45 N, 6.23; S, 14.20. Mp: 152 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(CN) 2204 (br); ν(CO, C═C) 1643, 1626. ^1H NMR: δ 1.53 (s, 18 H, ^{t}Bu), 2.39 (s, 6 H, Me).

Compound 1b. Yield: 78%. Anal. Calcd for $C_{16}H_{24}N_2O_2PtS_2$: C, 35.88; H, 4.52; N, 5.23; S, 11.97. Found: C, 35.87; H, 4.62; N, 5.43; S, 11.77. Mp: 184 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(CN) 2211, 2190; ν(CO, C═C) 1649, 1636. ^1H NMR: δ 1.54 (s, 18 H, ^{t}Bu), 2.39 (s, 6 H, Me).

Compound 2a. Yield: 75%. Anal. Calcd for $C_{24}H_{24}N_2O_2PdS_2$: C, 53.09; H, 4.46; N, 5.16; S, 11.81. Found: C, 52.77; H, 4.47; N, 5.15; S, 11.58. Mp: 168 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(CN) 2168; ν(CO, C═C) 1660, 1620. ^1H NMR: δ 2.40 [s, 6 H, C(O)*Me*], 2.43 [s, 12 H, Me (Xy)], 7.13−7.31 (m, 6 H, C_6H_3).

Compound 2b. Yield: 77%. Anal. Calcd for $C_{24}H_{24}N_2O_2PtS_2$: C, 45.63; H, 3.83; N, 4.43; S, 10.15. Found: C, 45.44; H, 3.69; N, 4.36; S, 9.69. Mp: 275 °C. Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(CN) 2193, 2160; ν(CO, C═C) 1680, 1619. ^1H NMR: δ 2.42 [s, 18 H, Me {Xy + C(O)Me}], 7.16−7.30 (m, 6 H, C_6H_3). Crystals of **2b** suitable for an X-ray diffraction study grew from CH_2Cl_2 and diethyl ether by the liquid diffusion method.

$[\{Pt(CN^tBu)_2\}_2Ag_2\{\mu^2,\eta^2-(S,S')-\{S_2C{=}C\{C(O)Me\}_2\}_2\}](ClO_4)_2$ (3). To a solution of **1b** (557.0 mg, 1.04 mmol) in acetone (60 mL) was added solid $AgClO_4$ (215.8 mg, 1.04 mmol), and the reaction mixture was stirred for 1.5 h. The resulting suspension was concentrated (3 mL) and Et_2O (80 mL) added to complete precipitation of **3** as a white solid that was filtered, washed with Et_2O (5 mL), and suction dried. Yield: 735 mg, 95%. Anal. Calcd for $C_{32}H_{48}Ag_2Cl_2N_4O_{12}Pt_2S_4$: C, 25.87; H, 3.26; N, 3.77; S, 8.63. Found: C, 25.67; H, 3.23; N, 3.93; S, 8.73. Mp: 132 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 225. IR (cm^{-1}): ν(CN) 2236, 2219; ν(CO, C═C) 1700, 1637, 1536; ν(ClO), 1087; δ(OClO), 623. ^1H NMR: δ 1.59 (s, 36 H, ^{t}BuNC), 2.48 (s, 12 H, Me).

$[M\{\eta^2-(S,S')-S_2C{=}C\{C(O)Me\}\}(CNR)\{C(NEt_2)(NHR)\}]$ [R = ^{t}Bu, M = Pd (4a), Pt (4b); R = Xy, M = Pd (5a), Pt (5b)]. To a solution of the appropriate $[\{M\{\eta^2-(S,S')-S_2C{=}C\{C(O)Me\}_2\}-(CNR)_2]$ complex (ca. 0.20 mmol) in CH_2Cl_2 (30 mL) was added the equimolar amount of $NHEt_2$. The solution was stirred for 15 h and concentrated to 2 mL. Et_2O (40 mL) was added to precipitate a cream solid, which was filtered, washed with Et_2O (5 mL), and suction dried.

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Compound 4a. Yield: 98%. Anal. Calcd for $C_{20}H_{35}N_3O_2PdS_2$: C, 46.19; H, 6.78; N, 8.08; S, 12.33. Found: C, 46.11; H, 7.08; N, 8.19; S, 11.83. Mp: 135 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3359; ν(CN) 2190; ν(CO, C═C) 1663, 1606, 1526. ^{1}H NMR (200 MHz, 25 °C): δ 1.15 ("t", $\mathrm{AB}X_3$, 3 H, CH2*Me*, $^{\mathrm{J}}{}_{\mathrm{HH}}$ = 7 Hz), 1.31 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 1.47 (s, 9 H, ^{t}Bu), 1.70 (s, 9 H, ^{t}Bu), 2.35 [s, 3 H, C(O)*Me*], 2.45 [s, 3 H, C(O)*Me*], 3.02 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.28 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.09 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.82 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 5.67 (s, 1 H, NH). ^{1}H NMR (+50 °C): 1.22 (m, $\mathrm{AB}X_3$, 6 H, CH$_2$*Me*), 1.42 (s, 9 H, ^{t}Bu), 1.70 (s, 9 H, ^{t}Bu), 2.38 [s, 6 H, C(O)*Me*], 3.00 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.27 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.13 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.74 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$) 5.66 (s, 1 H, NH). ^{1}H NMR (−50 °C): 1.15 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 1.30 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, JHH = 7 Hz), 1.50 (s, 9 H, ^{t}Bu), 1.71 (s, 9 H, ^{t}Bu), 2.35 [s, 3 H, C(O)*Me*], 2.53 [s, 3 H, C(O)*Me*], 3.10 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.30 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.97 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.96 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 5.70 (s, 1 H, NH). Crystals of **4a** suitable for an X-ray diffraction study grew from CH_2Cl_2 and Et_2O by the liquid diffusion method.

Compound 4b. Yield: 96%. Anal. Calcd for $C_{20}H_{35}N_3O_2PtS_2$: C, 39.58; H, 6.26; N, 7.13; S, 9.75. Found: C, 39.46; H, 5.80; N, 6.90; S, 10.23. Mp: 142 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3376, ν(CN) 2182; ν(CO, C═C) 1666, 1608, 1530. ^{1}H NMR (200 MHz, 25 °C): δ 1.17 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 1.29 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 1.46 (s, 9 H, ^{t}Bu), 1.72 (s, 9 H, ^{t}Bu), 2.32 [s, 3 H,C(O)*Me*], 2.47 [s, 3 H,C(O)*Me*], 3.04 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.31 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.13 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.92 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 5.77 (s, 1 H, NH, J_{PtH} = 86 Hz). ^{1}H NMR (+50 °C): 1.28 ("t", $\mathrm{AB}X_3$, 6 H, CH$_2$*Me*), 1.45 (s, 9 H, ^{t}Bu), 1.72 (s, 9 H, ^{t}Bu), 2.37 [s, 6 H, C(O)*Me*], 3.00 (m, $AB\mathrm{X}_3$, 4 H, CH$_2$), 5.77 (s, 1 H, NH, $\mathrm{J}_{\mathrm{PtH}}$ = 88 Hz). ^{1}H NMR (−50 °C): 1.17 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*), 1.28 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*), 1.48 (s, 9 H, ^{t}Bu), 1.72 (s, 9 H, ^{t}Bu), 2.34 [s, 3 H,C(O)*Me*], 2.54 [s, 3 H, C(O)*Me*], 3.05 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.32 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.95 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 5.06 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 5.79 (s, 1 H, NH, J_{PtH} = 84 Hz). Crystals of **4b** suitable for an X-ray diffraction study grew from CH_2Cl_2 and Et_2O by the liquid diffusion method.

Compound 5a. Yield: 94%. Anal. Calcd for $C_{28}H_{35}N_3O_2PdS_2$: C, 54.58; H, 5.73; N, 6.82; S, 10.41. Found: C, 54.77; H, 5.76; N, 6.90; S, 10.02. Mp: 158 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3249, ν(CN) 2165, ν(CO, C═C) 1678, 1597, 1530. ^{1}H NMR (200 MHz, 25 °C): δ 1.33 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 1.43 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 2.11 [s, 3 H, C(O)*Me*], 2.25 [s, 6 H, Me (Xy)], 2.29 [s, 6 H, Me (Xy)], 2.42 [s, 3 H, C(O)*Me*], 2.94 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.57 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.14 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.69 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 6.90 (m, 1 H, NH), 7.08−7.43 (m, 6 H, C_6H_3). ^{1}H NMR (+ 50 °C): 1.29−1.48 (m, $\mathrm{AB}X_3$, 6 H, CH$_2$*Me*), 2.26 [s, 6 H, Me (Xy)], 2.27 [s, br, 6 H, C(O)*Me*], 2.29 [s, 6 H, Me (Xy)], 2.96 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.51 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.21 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.65 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 7.08−7.43 (m, 7 H, C_6H_3 + NH). ^{1}H NMR (−50 °C): 1.31−1.42 (m, $\mathrm{AB}X_3$, 6 H, CH$_2$*Me*), 2.06 [s, 3 H, C(O)*Me*], 2.21 [s, 3 H, Me (Xy)], 2.25 [s, 9 H, Me (Xy)], 2.40 [s, 3 H, C(O)*Me*], 2.87 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 3.55 (m, $AB\mathrm{X}_3$, 2 H, CH$_2$), 4.05 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.72 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 6.88 ["t", 0.5 H, NH], 7.13−7.40 (m, 6 H, C_6H_3), 7.97 (s, br, 0.5 H, NH).

Compound 5b. Yield: 89%. Anal. Calcd for $C_{28}H_{35}N_3O_2PtS_2$: C, 47.72; H, 5.01; N, 5.96; S, 9.10. Found: C, 47.87; H, 5.04; N, 6.17; S, 8.77. Mp: 236 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 2. IR (cm^{-1}): ν(NH) 3263, ν(CN) 2155; ν(CO, C═C) 1680, 1601, 1530. ^{1}H NMR (200 MHz, 25 °C): δ 1.34 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 1.42 ("t", $\mathrm{AB}X_3$, 3 H, CH$_2$*Me*, J_{HH} = 7 Hz), 2.06 [s, 3 H, C(O)*Me*], 2.20 [s, 6 H, Me (Xy)], 2.26 [s, 3 H, Me (Xy)], 2.28 [s, 3 H, Me (Xy)], 2.40 [s, 3 H, C(O)*Me*], 3.59 (m, $AB\mathrm{X}_3$, 2 H, CH$_2$), 4.19 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.78 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 6.85 ["t", 0.5 H, NH, J_{NH} = 9 Hz), 7.06−7.23 (m, 6 H, C_6H_3), 7.46 (s, 0.5 H, NH). ^{1}H NMR (+55 °C): 1.34−1.47 (m, $\mathrm{AB}X_3$, 6 H, CH$_2$*Me*), 2.22 [s, 6 H, Me (Xy)], 2.27 [s, br, 6 H, C(O)Me], 2.29 [s, 6 H, Me (Xy)], 3.52 (m, br, $AB\mathrm{X}_3$, 2 H, CH$_2$), 4.29 (m, br, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.73 (m, br, $AB\mathrm{X}_3$, 1 H CH$_2$], 6.92−7.40 (m, 7 H, NH + C_6H_3). ^{1}H NMR (−50 °C): 1.21−1.44 (m, $\mathrm{AB}X_3$, 6 H, CH$_2$*Me*), 2.02 [s, 3 H, C(O)*Me*], 2.21 [s, 9 H, Me (Xy)], 2.27 [s, 3 H, Me (Xy)], 2.41 [s, 3 H, C(O)*Me*], 3.55 (m, $AB\mathrm{X}_3$, 2 H, CH$_2$), 4.10 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 4.79 (m, $AB\mathrm{X}_3$, 1 H, CH$_2$), 6.84 ["t", 0.5 H, NH, J_{NH} = 9 Hz], 7.10−7.40 (m, 6 H, C_6H_3), 7.92 (s, 0.5 H, NH).

[M{η^2-(*S,S′*)-S_2C═C{C(O)Me}$_2$}(CN^{t}Bu){C(NH$_2$)(NH^{t}Bu)}] [M = Pd (6a), Pt (6b)]. NH_3 was bubbled through a solution of **1a** (250 mg, 0.56 mmol) or **1b** (286.0 mg, 0.53 mmol) in THF (60 mL) for 1 h. The resulting solution was stirred for 15 h and concentrated under vacuum (3 mL), and Et_2O (60 mL) was added to precipitate a cream solid that was filtered, washed with Et_2O (2 × 10 mL), and suction dried. Compound **6a** is hygroscopic and must be filtered and dried under nitrogen.

Compound 6a. Yield: 235 mg, 91%. Anal. Calcd for $C_{16}H_{27}N_3O_2PdS_2$: C, 41.42; H, 5.87; N, 9.06; S, 13.82. Found: C, 41.13; H, 5.91; N, 9.34; S, 13.56. Mp: 149 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3430, 3205; ν(CN) 2200; ν(CO, C═C) 1684, 1616. ^{1}H NMR (d_6-DMSO): δ 1.44 (s, 9 H, ^{t}Bu), 1.45 (s, 9 H, ^{t}Bu), 1.50 (s, 9 H, ^{t}Bu), 1.52 (s, 9 H, ^{t}Bu), 2.07 [s, 6 H, C(O)*Me*], 2.22 [s, 6 H, C(O)*Me*], 7.10 (s, 1 H, NH), 7.21 (s, 1 H, NH), 8.01 (s, 2 H, NH$_2$), 8.16 (s, 2 H, NH$_2$).

Compound 6b. Yield: 275 mg, 94%. Anal. Calcd for $C_{16}H_{27}N_3O_2PtS_2$: C, 34.78; H, 4.92; N, 7.60; S, 11.60. Found: C, 35.19; H, 5.05; N, 7.63; S, 11.50. Mp: 159 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3401,3315, 3269, 3228; ν(CN) 2183; ν(CO, C═C) 1681, 1627, 1588. ^{1}H NMR (d_6−DMSO): δ 1.26 (s, 9 H, ^{t}Bu), 1.42 (s, 9 H, ^{t}Bu), 1.45 (s, 9 H, ^{t}Bu), 1.53 (s, 9 H, ^{t}Bu), 2.14 [s, 3 H, C(O)*Me*], 2.16 [s, 3 H, C(O)*Me*], 2.21 [s, 6 H, C(O)*Me*], 7.27 (s, 1 H, NH), 7.38 (s, 1 H, NH), 7.89 (s, 2 H, NH$_2$), 8.09 (s, 2 H, NH$_2$).

[M{η^2-(*S,S′*)-S_2C═C{C(O)Me}$_2$}{C(NH$_2$)(NHXy)}$_2$] [M = Pd (7a), Pt (7b)]. NH_3 was bubbled through a solution of **2a** (227.0 mg, 0.51 mmol) or **2b** (422.8 mg, 0.67 mmol) in THF (60 mL) for 1 h. A precipitate immediately formed. The suspension was stirred for 15 h and filtered and the cream solid washed with Et_2O (3 × 10 mL) and suction dried.

Compound 7a. Yield: 245.0 mg, 83%. Anal. Calcd for $C_{24}H_{30}N_4O_2PdS_2$: C, 49.96; H, 5.24; N, 9.71; S, 11.11. Found: C, 49.93; H, 5.29; N, 9.74; S, 11.03. Mp: 187 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3380, 3273, 3182; ν(CO, C═C) 1690, 1635, 1557. ^{1}H NMR (d_6-DMSO): δ 2.10 [s, 12 H, Me (Xy)], 2.24 [s, 6 H, C(O)*Me*], 6.77 (s, 2 H, NH$_2$), 7.13 (m, 6 H, C_6H_3), 7.81 (s, 2 H, NH$_2$), 9.48 (s, 2 H, NH). ^{13}C{^{1}H} NMR: δ 17.72 [s, Me (Xy)], 31.80 [s, C(O)*Me*], 127.69 (s, *p*-CH, Xy), 128.26 (s, *m*-CH, Xy), 134.02 (s, *ipso*-C, Xy), 135.45 (s, *o*-C, Xy), 139.51 [s, *C*═S$_2$], 195.33 [s, C═*C*S$_2$], 196.89 (s, Pd*C*N$_2$), 198.38 (s, *C*O). ^{13}C-DEPT{1H} NMR: δ 21.26 [s, Me (Xy)], 35.34 [s, C(O)*Me*], 131.28 (s, *p*-CH, Xy), 131.83 (s, *m*-CH, Xy).

Compound 7b. Yield: 410 mg, 92%. Anal. Calcd for $C_{24}H_{30}N_4O_2PtS_2$: C, 43.30 H, 4.54; N, 8.42; S, 9.63. Found: C, 43.70; H, 4.79; N, 8.36; S, 9.27. Mp: 205 °C (dec). Λ_M (Ω^{-1} cm^2 mol^{-1}): 0. IR (cm^{-1}): ν(NH) 3392, 3265, 3179; ν(CO, C═C) 1686, 1606, 1550. ^{1}H NMR (d_6-DMSO): δ 2.09 [s, 12 H, Me (Xy)], 2.24 [s, 6

Table 1. Crystal Data for Compounds **2b**, **4a**, and **4b**

	2b	**4a**	**4b**
formula	$C_{24}H_{24}N_2O_2PtS_2$	$C_{20}H_{35}N_3O_2PdS_2$	$C_{20}H_{35}N_3O_2PtS_2$
cryst habit	yellow tablet	yellow tablet	yellow tablet
cryst size (mm^3)	0.20 × 0.20 × 0.11	0.32 × 0.21 × 0.15	0.16 × 0.15 × 0.10
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a (Å)	9.5174(6)	12.3951(8)	12.3844(8)
b (Å)	11.3869(6)	8.6027(6)	8.6170(6)
c (Å)	12.1696(8)	22.6438(16)	22.6190(14)
α (deg)	70.409(3)	90	90
β (deg)	76.920(3)	99.750(3)	99.858(3)
γ (deg)	74.938(3)	90	90
V (Å^3)	1185.71(12)	2379.7(3)	2378.2(3)
Z	2	4	4
ρ_{calcd} (Mg m^{-3})	1.769	1.452	1.700
M_r	631.66	520.03	608.72
λ (Å)	0.71073	0.71073	0.71073
T (K)	143(2)	143(2)	143(2)
F(000)	616	1080	1208
μ Mo Kα (mm^{-1})	6.1	0.98	6.1
θ range (deg)	1.8−30	1.7−30	1.7−30
abs corr	face indexing	face indexing	face indexing
reflns coll	19060	49246	48996
indep reflns	6876	6960	6958
R_{int}	0.050	0.053	0.063
transm	0.567/0.269	0.872/0.793	0.527/0.336
data/restraints/params	6876/78/286	6960/0/267	6958/0/267
R1 [$I > 2\sigma(I)$]	0.0211	0.0210	0.0210
wR2 (all reflns)	0.0427	0.0509	0.0437
max $\Delta\rho$/e Å^{-3}	0.82	0.49	0.97
$S(F^2)$	1.00	1.05	1.00

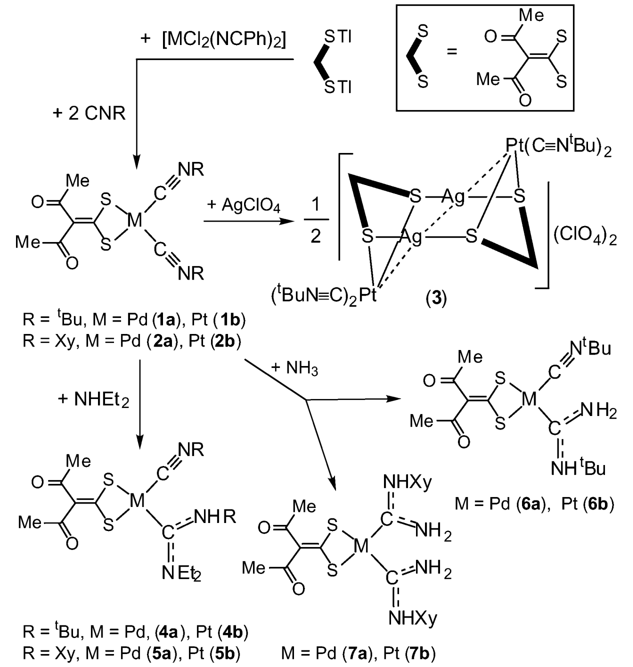
H, C(O)*Me*], 6.85 (s, 2 H, NH_2), 7.12 (m, 6 H, C_6H_3), 7.68 (s, 2 H, NH_2), 9.36 (s, 2 H, NH).

X-ray Structure Determinations. Numerical data are presented in Table 1. Crystals were mounted on glass fibers and transferred to the cold gas stream of the diffractometer (Bruker SMART 1000 CCD). Data were recorded with Mo Kα radiation (λ = 0.71073Å) in ω- and ϕ-scan mode. Absorption corrections were based on indexed faces. Structures were refined anisotropically on *F*2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using a riding model or with rigid methyl groups. Special features of refinement include the following: For **4a** and **4b** (which are isostructural), the NH hydrogens were refined freely; the methyl groups at C(4) were poorly resolved and may be rotationally disordered. The latter applies also to C(17) of compound **2b**.

Results and Discussion

Synthesis. Complexes [M{η^2-S_2C=C{C(O)Me}$_2$}(CNR)$_2$] [R = ^{t}Bu, M = Pd (**1a**), Pt (**1b**); R = Xy, M = Pd (**2a**), Pt (**2b**)] were obtained, together with TlCl, by reacting in CH_2Cl_2 [Tl_2{S_2C=C{C(O)Me}$_2$}]$_n$[40] with the appropriate [$MCl_2(NCPh)_2$] complex and RNC in a 1:1:2 molar ratio (see Scheme 1). They could also be obtained in similar yields by reacting the polymeric species [M{S_2C=C{C(O)Me}$_2$}]$_n$ with RNC (1:2).[41] Compound **1b** can act as a ligand toward $AgClO_4$ to give the tetranuclear complex [{Pt(CN^{t}Bu)$_2$}$_2$Ag$_2$-{μ^2,η^2-(*S*,*S*′)-{S_2C=C{C(O)Me}$_2$}$_2$}](ClO_4)$_2$ (**3**), as we have shown for other [M{η^2-S_2C=C{C(O)Me}$_2$}L$_2$] derivatives (M = Pd, Pt, L = PPh_3; M = Pt, L$_2$ = cod).[41] The reaction was carried out in acetone, and diethyl ether was used to precipitate the complex in almost quantitative yield. The nucleophilic attack of NH_nR_{3-n} ($n \geq 1$) species on isocyanide ligands to give carbene complexes is well documented.[48−54] The isocyanide complexes **1** and **2** reacted with diethylamine or ammonia to give carbene complexes **4**−**7** in excellent yields (Scheme 1). When $NHEt_2$ was used, complexes [M{η^2-S_2C=C{C(O)Me}$_2$}(CNR){C(NEt_2)(NHR)}] [R =

Scheme 1



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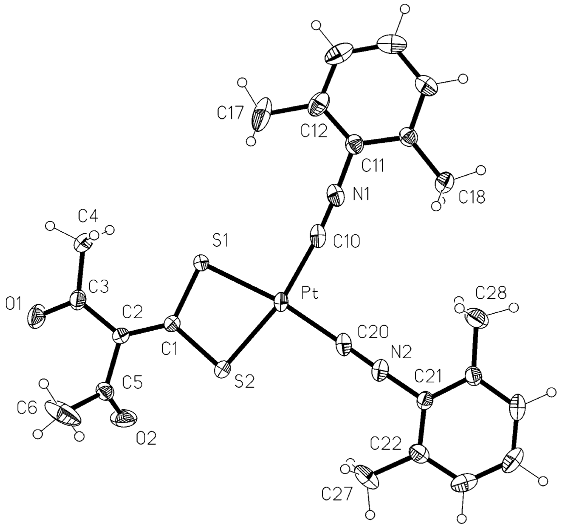


Figure 1. Structure of complex **2b** in the crystal. Ellipsoids represent 50% probability levels. Selected bond lengths (Å) and angles (deg): Pt−C(10) 1.957(2), Pt−C(20) 1.959(2), Pt−S(1) 2.3022(5), Pt−S(2) 2.3139(5), S(1)−C(1) 1.7536(19), S(2)−C(1) 1.766(2), O(1)−C(3) 1.219(2), O(2)−C(5) 1.201(3), N(1)−C(10) 1.152(3), N(1)−C(11) 1.401(3), N(2)−C(20) 1.151(3), N(2)−C(21) 1.393(3), C(10)−Pt−C(20) 94.93(9), C(10)−Pt−S(1) 93.14(6), C(20)−Pt−S(2) 96.73(6), S(1)−Pt−S(2) 75.210(18), C(1)−S(1)−Pt 89.55(7), C(1)−S(2)−Pt 88.88(6), C(10)−N(1)−C(11) 175.3(2), C(20)−N(2)−C(21) 178.4(2), C(2)−C(1)−S(1) 128.93(16), C(2)−C(1)−S(2) 124.72(15), S(1)−C(1)−S(2) 106.34(10), C(1)−C(2)−C(3) 127.23(18), C(1)−C(2)−C(5) 119.15(18), C(3)−C(2)−C(5) 113.59(17), O(1)−C(3)−C(2) 119.0(2), O(1)−C(3)−C(4) 119.0(2), C(2)−C(3)−C(4) 122.03(18), O(2)−C(5)−C(6) 119.8(2), O(2)−C(5)−C(2) 122.31(18), C(6)−C(5)−C(2) 117.9(2), N(1)−C(10)−Pt 173.94(19), N(2)−C(20)−Pt 178.66(19).

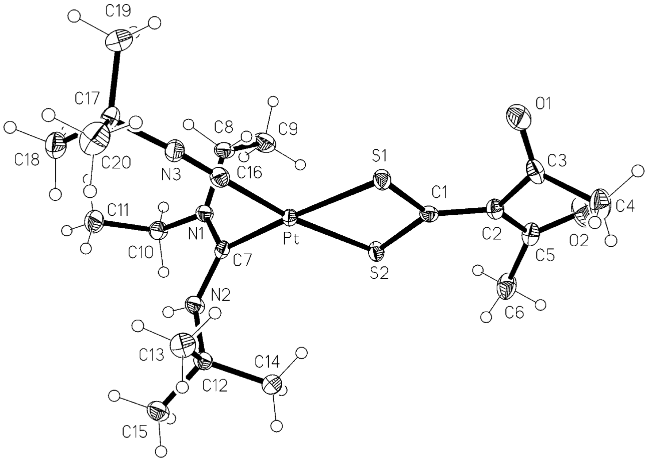
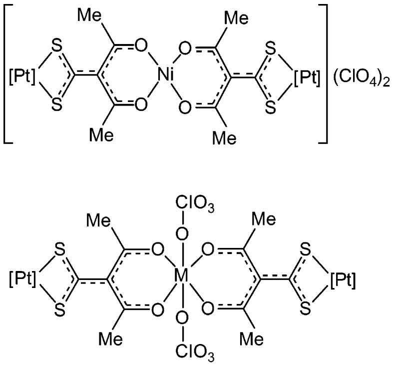


Figure 2. Structure of complex **4b** in the crystal. Ellipsoids represent 50% probability levels. Selected bond lengths (Å) and angles (deg): Pt−C(16) 1.936(2), Pt−C(7) 2.053(2), Pt−S(2) 2.3208(5), Pt−S(1) 2.3331(5), S(1)−C(1) 1.748(2), S(2)−C(1) 1.758(2), N(1)−C(7) 1.345(3), N(1)−C(10) 1.465(3), N(1)−C(8) 1.481(2), N(2)−C(7) 1.334(3), N(2)−C(12) 1.492(3), N(3)−C(16) 1.148(3), N(3)−C(17) 1.463(3), C(1)−C(2) 1.381(3), C(16)−Pt−C(7) 88.31(8), C(7)−Pt−S(2) 98.20(5), C(16)−Pt−S(1) 98.88(6), S(2)−Pt−S(1) 74.427(18), C(1)−S(1)−Pt 89.26(7), C(1)−S(2)−Pt 89.41(7), C(7)−N(1)−C(10) 122.93(17), C(7)−N(1)−C(8) 122.45(17), C(10)−N(1)−C(8) 113.93(16), C(7)−N(2)−C(12) 130.54(18), C(16)−N(3)−C(17) 172.7(2), C(2)−C(1)−S(1) 124.71(16), C(2)−C(1)−S(2) 128.48(16), S(1)−C(1)−S(2) 106.81(11), C(1)−C(2)−C(5) 125.78(19), C(1)−C(2)−C(3) 119.07(18), C(5)−C(2)−C(3) 115.13(18), N(2)−C(7)−N(1) 116.06(18), N(2)−C(7)−Pt 124.37(15), N(1)−C(7)−Pt 119.55(14), N(1)−C(8)−C(9) 113.29(18), N(1)−C(10)−C(11) 112.32(18). Selected bond lengths (Å) and angles (deg) for the isostructural **4a**: Pd−C(16) 1.9783(12), Pd−C(7) 2.0679(11), Pd−S(2) 2.3112(3), Pd−S(1) 2.3216(3), S(1)−C(1) 1.7450(12), S(2)−C(1) 1.7560(12), N(1)−C(7) 1.3394(15), N(1)−C(10) 1.4717(15), N(1)−C(8) 1.4767(15), N(2)−C(7) 1.3342(15), N(2)−C(12) 1.4918(15), N(3)−C(16) 1.1502(16), N(3)−C(17) 1.4648(15), O(1)−C(3) 1.2159(16), O(2)−C(5) 1.2330(16), C(1)−C(2) 1.3796(15), C(16)−Pd−C(7) 88.27(5), C(7)−Pd−S(2) 98.08(3), C(16)−Pd−S(1) 98.65(3), S(2)−Pd−S(1) 74.741(11), C(1)−S(1)−Pd 89.12(4), C(1)−S(2)−Pd 89.19(4), C(7)−N(1)−C(10) 122.93(10), C(7)−N(1)−C(8) 122.26(10), C(10)−N(1)−C(8) 114.16(9), C(7)−N(2)−C(12) 129.54(10), C(16)−N(3)−C(17) 173.95(12), C(2)−C(1)−S(1) 124.91(9), C(2)−C(1)−S(2) 128.22(9), S(1)−C(1)−S(2) 106.87(6), C(1)−C(2)−C(5) 126.09(11), C(1)−C(2)−C(3) 119.00(10), C(5)−C(2)−C(3) 114.89(10), N(2)−C(7)−N(1) 116.59(10), N(2)−C(7)−Pd 124.75(9), N(1)−C(7)−Pd 118.64(8), N(1)−C(8)−C(9) 113.31(10), N(3)−C(16)−Pd 174.49(11).

Chart 1



[Pt] = Pt(PPh_3)$_2$; M = Cu, Cd

^{t}Bu, M = Pd (**4a**), Pt (**4b**); R = Xy, M = Pd (**5a**), Pt (**5b**)], resulting from the attack of only one of the isocyanide ligands, could be obtained. The same complexes resulted, even in the presence of a large excess of amine, regardless of the nature of the isocyanide. However, when NH_3 was bubbled through solutions of the same complexes in THF, different results were obtained, depending on the isocyanide. Thus, while complexes **1a** and **1b**, containing ^{t}BuNC, reacted with ammonia to give mixed isocyanide−carbene complexes **6a** and **6b**, their homologues with XyNC gave bis(carbene) complexes **7a** and **7b.** The isolation of complexes **6** needed concentration of the THF solutions and addition of Et_2O, whereas complexes **7** precipitated in THF. Complex **6a** is very hygroscopic and needs to be handled and stored under a nitrogen atmosphere. The reactions leading to complexes **4**−**7** seem to depend on steric factors because complexes with two carbene ligands {C(NR_2)(NHR′)} only form for the smaller R (H < Et) and R′ (Xy < ^{t}Bu) sustituents.

Crystal Structures of Complexes. The crystal structures of **2b** (Figure 1), **4a**, and the isostructural **4b** (Figure 2) have been determined, and they all display one chelating *Z,E*-2,2-diacetyl-1,1-ethylenedithiolato ligand coordinated through the sulfur atoms. We have found the same conformation and coordination mode in most other 2,2-diacetyl-1,1-ethylenedithiolato complexes studied by us.[39,41,42] Exceptions are the coordination through sulfur and oxygen atoms in complexes [{Pt(PPh_3)$_2$}$_2$Ni{μ^2-(O,O′),η^2-(*S*,*S*′)-S_2C=C{C(O)Me}$_2$}$_2$](ClO_4)$_2$ and [{Pt(PPh_3)$_2$}$_2${M($OClO_3$)$_2$}{μ^2-(O,O′),η^2-(*S*,*S*′)-S_2C=C{C(O)Me}$_2$}$_2$] (M = Cu, Cd) (see Chart 1) and the *E,E* conformation found for the dithiolene ligand in the crystal structure of the Pt_2Cu complex.[42] Two XyNC ligands (**2b**) or one ^{t}BuNC and one C(NEt_2)(NH^{t}Bu) ligands (**4a**

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(52) Bonatti, F.; Minghetti, G. *J. Organomet. Chem.* **1973**, *59*, 403.

(53) Minghetti, G.; Baratto, L.; Bonatti, F. *J. Organomet. Chem.* **1975**, *102*, 397.

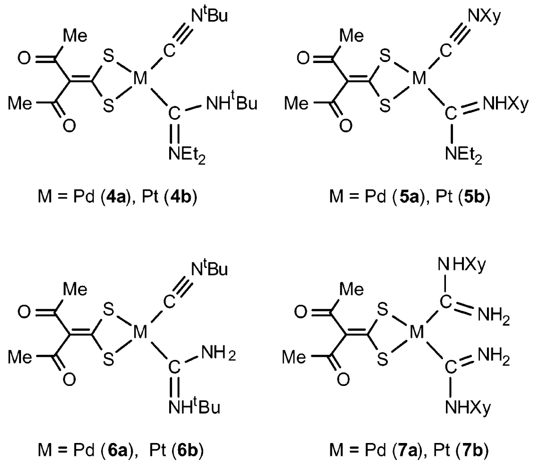
(54) McCleverty, J. A.; Da Mota, M. M. M. *J. Chem. Soc., Dalton Trans.* **1973**, 2571.

and **4b**) complete a distorted square planar environment for the metal. The mean deviation for the S(1)S(2)MC(10)C(20) plane in **2b** or S(1)S(2)MC(7)C(16) in **4a** and **4b** is 0.104, 0.023, or 0.020 Å, respectively, and the S(1)MS(2) angle [75.210(8)° (**2b**), 74.741(11)° (**4a**), 74.427(18)° (**4b**)] is narrow, reflecting the small bite of the chelating ligand which is essentially planar [mean deviation for the S(1)−S(2)−C(1)−C(2)−C(3)−C(5) plane 0.017 (**2b**), 0.005 (**4a**), and 0.006 (**4b**) Å]. Both acetyl groups are rotated out of the C(1)−C(2)−C(3)−C(5) plane (**2b**, 57.5°, 10.7°; **4a**, 46.3°, 22.5°; **4b**, 46.7°, 21.9°) although in **2b** one of them only slightly. The olefinic C(1) and C(2) atoms are in distorted trigonal perfectly planar environments showing narrow S(1)−C(1)−S(2) angles [106.34(10)−106.87(6)°]. The C(1)−C(2) bond distances [**2b**, 1.366(3) Å; **4a**, 1.3796 (15) Å; **4b**, 1.381(3) Å] are similar or slightly longer than in most 2,2-diacetyl-1,1-ethylenedithiolato complexes of palladium, platinum,[41,42] or gold[40] [in the range 1.342(6)−1.374(6) Å] but shorter than in $[\{Pt(PPh_3)_2\}_2\{Cu(OClO_3)_2\}\{\mu^2\text{-}(O,O'),\eta^2\text{-}(S,S')\text{-}S_2C{=}C\{C(O)Me\}_2\}_2\}]$ [1.429(10) Å]. The M−S bond distances found in these complexes suggest a slight decrease of trans influence in the series $C(NEt_2)(NH^tBu)$ > ^tBuNC > XyNC.

The $C_{carbene}$−N bond distances in complexes **4a** [1.3394(15) and 1.3342(15) Å] and **4b** [1.345(3) and 1.334(3) Å] are not significantly different.

NMR Spectra. The ^1H NMR spectra of complexes **1**−**3** and **7** show one single resonance for all the 6 (**1**, **2**, **7**) or 12 (**3**) acetyl protons, indicating either an *E*,*E* or *Z*,*Z* conformation of the dithiolene ligands or, most likely, the fast rotation of the acetyl groups around the C−C(O)Me bond. In the ^1H NMR spectrum of **2b** a chance superposition of the resonances of the methyl groups of both the dithiolene and the XyNC ligands occur giving rise to a unique singlet of 18 protons at 2.42 ppm. This coincidence does not occur in the spectra of the remaining $[M\{S_2C{=}C\{C(O)Me\}_2\}(CNR)_2]$ complexes, which display separate resonances for the acetyl (**1a**, **b,** 2.39 ppm; **2a**, 2.40 ppm) and isocyanide methyl protons (**1a**, 1.53 ppm; **1b**, 1.54 ppm; **2a**, 2.43 ppm). The same applies to complex **3** which shows two singlets at 2.48 [C(O)Me] and 1.59 (^tBu) ppm.

Scheme 2



M = Pd (**4a**), Pt (**4b**)

M = Pd (**5a**), Pt (**5b**)

M = Pd (**6a**), Pt (**6b**)

M = Pd (**7a**), Pt (**7b**)

The multiple character of the C−N bonds in the carbene ligands of complexes **4**−**7** may induce the existence of *Z* and *E* isomers. Room-temperature ^1H NMR spectra of complexes **4a** and **4b** show resonances due to two inequivalent ABX_3 systems corresponding to the ethyl groups, two singlets (**4a**, 1.47, 1.70 ppm; **4b**, 1.46, 1.72 ppm) for the methyl protons of the ^tBu groups in the isocyanide and carbene ligands and a singlet due to the NH proton (**4a**, 5.67 ppm; **4b**, 5.77 ppm) indicating fast rotation around the ^tBuNH−C bond and slow rotation around the Et_2N−C bond and suggesting a greater bond order in the latter. In Scheme 2 is represented a limiting resonance form describing this bonding situation. The acetyl protons are observed as two singlets (**4a**, 2.35, 2.45 ppm; **4b**, 2.32, 2.47 ppm) indicating, most likely, the restricted rotation of the $C\{C(O)Me\}_2$ moiety around the C═C bond. At 50 °C, the spectrum of **4a** shows still inequivalent Et groups with a broad resonance for their Me protons at 1.20 ppm and considerably broadened resonances for the four inequivalent methylenic protons. In the ^1H NMR spectrum of **4b** at 50 °C, only one pseudotriplet (1.28 ppm) and one pseudoquartet (3.00 ppm) are observed, indicating free rotation around the $C{-}NEt_2$ bond. The NH resonance in complexes **4** is not affected by the temperature change. As mentioned, the $C_{carbene}$−N bond distances are not significantly different in the solid state, which implies that the different behavior of the NEt_2 could be due to a combination of steric and electronic effects. The greater inductive effect +I of two Et groups than that of an hydrogen and a ^tBu group favors a greater Et_2N−C bond order than that of a ^tBuHN−C bond.

In contrast, in complexes **5** and **6**, the rotation is restricted around the C−NHR moiety (Scheme 2). Thus, the room-temperature spectrum of **5b** shows the presence of both *Z* and *E* isomers (in 1:1 molar ratio) due to the restricted rotation around the C−NHXy bond. Two resonances are observed for each, the Me protons of the Xy group of the carbene ligand (singlets of similar intensity at 2.26 and 2.28 ppm) and the NH proton (a pseudotriplet at 6.85 ppm and a singlet at 7.46 ppm). However, while two resonances are observed for the Et groups of the *Z* and *E* isomers, only one is observed for the C(O)Me and Me (XyNC) groups. The low-temperature spectrum of **5b** (−50 °C) is similar to that at room temperature, with the exception of the superposition of the Me resonance of the XyNC ligand with that of the carbene of one of the isomers. When the temperature is raised to 55 °C, free rotation around the C−NHXy occurs, and only two resonances due to the Xy groups are observed. The two resonances assigned to the NH group in the *Z* and *E* isomers disappear, and the unique expected resonance appears included in the multiplet due to the arylic protons. The same situation is observed for the homologous complex **5a** with the difference that the *Z* and *E* isomers are only observed at low temperature, suggesting a lower activation energy for the rotation about the C−NHXy bond. Similarly, in the ^1H NMR spectra of complexes **6a** and **6b**, four resonances are observed for the ^tBu groups of the isocyanide and carbene ligands (**6a**, 1.44, 1.45, 1.50, 1.52; **6b**, 1.26, 1.42, 1.45, 1.53 ppm), proving the presence of both *Z* and *E* isomers in solution (Scheme 2). The different carbon donor ligands, carbene and isocyanide, render the methyl protons of the dithiolene ligand inequivalent, which should appear as four singlets, two for each of the isomers. However, only two [**6a**: 2.07, 2.22 ppm, 1:1 ratio] or three [**6b**: 2.14, 2.16, 2.21 ppm, 1:1:2 ratio] resonances are observed due to accidental coincidence of one or both pairs of signals. The N*H*^{t}Bu and NH_2 protons give four resonances in the region 7.1−8.2 ppm. The equivalence of both NH_2 protons in each isomer suggests that free rotation of the NH_2 group occurs around the $C-NH_2$ bond (Scheme 2).

In the ^{1}H NMR spectra of the bis(carbene) complexes **7a** and **7b**, the presence of three singlets (1:1:1) corresponding to NH protons and only one singlet for the methyl (Xy) protons proves the restricted rotation of the NH_2 group around the C−N bond and the free rotation of the NHXy group (Scheme 2).

IR Spectra. The IR spectra, measured in the solid state, show several bands in the 1700−1450 cm^{-1} region that cannot be unequivocally assigned to ν(C=O) or ν(C=C) stretching modes since these have proved to be coupled in other carbonyl-containing push−pull ethylenes.[5] The spectra of the carbene complexes **4**−**7** show also ν(C=N) bands in the same region. In complexes **1**−**5**, the presence of isocyanide ligands is evidenced by one band in the 2150−2220 cm^{-1} region while the carbene complexes show the ν(NH) bands in the 3430−3179 cm^{-1} region. Complex **3** shows two bands at 1087 and 623 cm^{-1} corresponding to the perchlorato anion.

Molar conductivities in acetone of the neutral complexes **1**−**2** and **4**−**7** are in the range 0−2 Ω^{-1} cm^2 mol^{-1} while that of the dicationic **3** is 225 Ω^{-1} cm^2 mol^{-1}, in agreement with its 2:1 electrolytic nature.[55]

Acknowledgment. We thank Ministerio de Ciencia y Tecnología, FEDER (BQU2001-0133), and the Fonds der Chemischen Industrie for financial support. S.H. thanks the Ministerio de Educación y Cultura (Spain) for a grant.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for complexes**2a**, **4a**, and **4b**. This material is available free of charge via the Internet at http://pubs.acs.org

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