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Thiosemicarbazone platinacycles with tertiary phosphines. Preparation of novel heterodinuclear platinum–tungsten complexes

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ABSTRACT

Treatment of thiosemicarbazones $(R^1C_6H_4)C(H){=}NN(H)C({=}S)NHR^2$ [R^1,R^2: 4-Me,H (**a**); 4-Me,Me (**b**); 4-Me,Et (**c**); 2-Me,H (**d**); 2-Me,Me (**e**); 2-Me,Et (**f**)] with *cis*-$[PtMe_2(cod)]$ afforded the tetranuclear platinum(II) compounds $[Pt\{(R^1C_6H_3)C(H){=}NN{=}C(S)NHR^2\}]_4$ (**1a**–**1f**) with the ligand as terdentate [*C*,*N*,*S*] after C–H activation and NH deprotonation. The reaction of **1a**–**1f** with PPh_3 in 1:4 M ratio gave the mononuclear compounds $[Pt\{(R^1C_6H_3)C(H){=}NN{=}C(S)NHR^2\}(PPh_3)]$ (**2a**–**2f**). Treatment of **1a**–**1f** with large-bite diphosphines $Ph_2P(CH_2)_nPPh_2$ ($n = 2$, dppe; $n = 3$, dppp; $n = 4$, dppb) afforded the dinuclear compounds $[\{Pt[(R^1C_6H_3)C(H){=}N{-}N = C(S)NHR^2]\}_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}]$, (**3a**–**3f**, **4a–4f**, **5a**–**5f**), with the diphosphine in a bridging mode. Similar reactions with the short-bite diphosphines $Ph_2PCH_2PPh_2$ (dppm) and $Ph_2PC({=}CH_2)PPh_2$ (vdpp) yielded the mononuclear compounds $[Pt\{(R^1C_6H_3)C(H){=}NN{=}C(S)NHR^2\}\text{-}(Ph_2PR^3PPh_2\text{-}P)]$ ($R^3 = CH_2$, **6a**–**6f**; $R^3 = C = CH_2$, **7a**–**7f**) with the diphosphine in a monodentate coordination. Treatment of **1a**–**1f** with $[W(CO)_5(Ph_2CH_2PPh_2)]$ gave the heterodinuclear species $[\{Pt[(R^1C_6H_3)C(H){=}NN{=}C(S)NHR^2]\}\{Ph_2CH_2PPh_2W(CO)_5\}]$ (**8a**–**8f**). The molecular structures of compounds **3e** and **5c** have been determined by X-ray crystal structure analysis.

1. Introduction

The cyclometallation reaction, i.e. the intramolecular activation of aromatic C–H bonds by transition metals in coordinated ligands, has been extensively researched, especially in the case of metallated phenyl rings [1]. The main interest in this type of compounds stems from their noteworthy applications in organic and organometallic synthesis [2], as active catalysts [3], liquid crystals [4], for the design of potential biologically active materials [5] or for their photochemical properties [6]. In particular, platinacycles containing nitrogen, phosphorus or sulfur donor atmos [7] also offer attractive applications as catalysts in Michael and Diels–Alder reactions for C–C bond formation [8]. Recently, platinum species have represented an important class of complexes particularly from the point of view of their luminescent properties, and the usage of the phosphorescent complexes as emitters in light-emitting diodes (LEDS) [9]. These findings strongly bring forth the need to advance in the search for novel complexes which may be suitable for any of the above mentioned applications. This enhances the importance of the processes leading to the design, preparation and characterization of innovative metallacycles which will break new ground, a challenge to be achieved by changing the nature of the metal, modifying the metallated ligand and/or the ancilliary ligands, or the three altogether. In particular, thiosemicarbazones and semicarbazones have been known to form stable complexes with many transition metal ions [10]. Treatment of the appropriate ligands with $Li_2[PdCl_4]$ or $K_2[PtCl_4]$ usually gives chloro-bridged dinuclear complexes, although mononuclear species with terminal halogen ligands are also known [11]. Our interest in cyclometallated compounds has been, in part, focused on the study of complexes derived from [*C*,*N*,*S*] terdentate ligands such as thiosemicarbazones or Schiff base ligands with additional sulfur donor atoms, which react readily with $M_2[PdCl_4]$ (M = Li, K), $Pd(OAc)_2$ or $K_2[PtCl_4]$ to give mono- or tetra-nuclear compounds [12]. We have shown that in thiosemicarbazone palladacycles the organic ligand binds tightly to the metal as terdentate [*C*,*N*,*S*] in a tetranuclear [13] structure through $M{-}S_{chelating}$ and $M{-}S_{bridging}$ bonds. The strength of the former bond is put forward in reactions with nucleophiles, where even treatment with strong chelating tertiary diphosphines yields complexes with the ligand in a [*C*,*N*,*S*] fashion and a mono-coordinated diphosphine, to render bidentate [*P*,*S*] palladacycle metalloligands: they are starting materials for the preparation of dinuclear assemblies [14]. Similar cycloplatinated species which were hitherto unknown are describe herein, together with heterodinuclear platinacycles where the second metal binds solely through the

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phosphorus atom, as opposed to the [*P*,*S*] coordination mode mentioned above.

2. Results and discussion

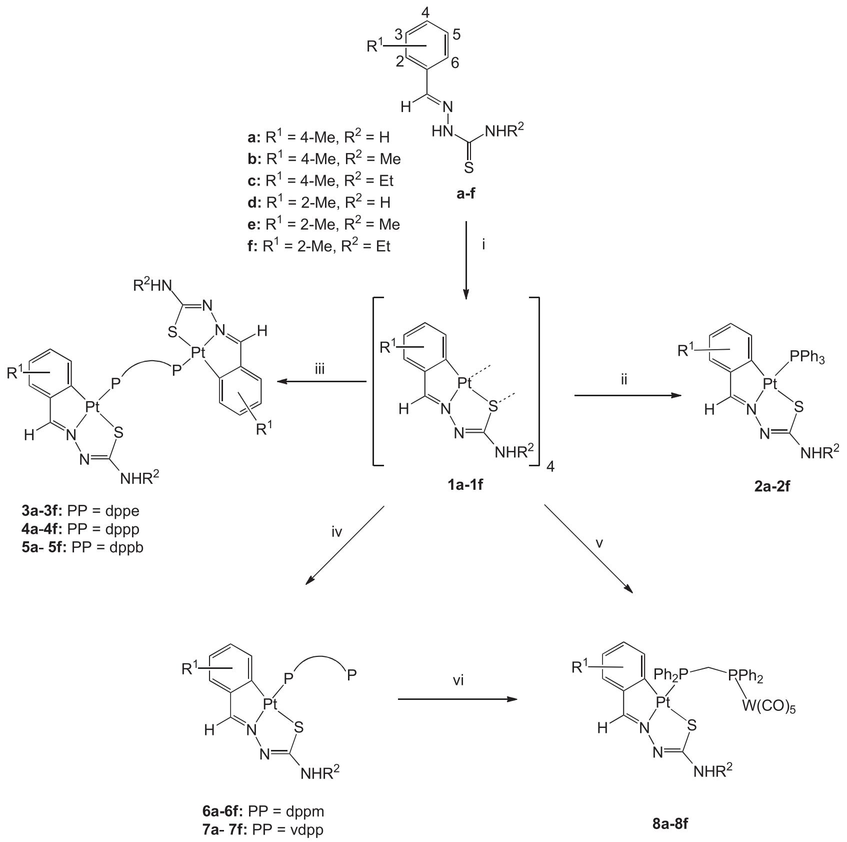
For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N, S), and by IR and ^1H, $^{31}P-\{^1H\}$ and (in part) $^{13}C-\{^1H\}$ NMR spectroscopy.

Thiosemicarbazones derived from aromatic aldehydes are less prone to cyclometallation as opposed to the analogous ketone derivatives, with few examples having been hitherto reported [15]; to the best of our knowledge the corresponding platinacycles with short bite diphosphines remained outstanding. We first sought out to prepare the ligands by the classical condensation method. Thus, **a**–**f** were obtained accordingly as air-stable solids by the reaction of 4-methylbenzaldehyde or 2-methylbenzaldehyde with the compound methyl-thiosemicarbazide or ethyl-thiosemicarbazide (complexes **a** and **d**), as appropriate and were fully characterized (see Section 4). The ensuing ligands were metallated in good yield by treatment with [*cis*-$PtMe_2$(COD)], as opposed to the $K_2[PdCl_4]$ salt used in previous preparations; this greatly reduces the reaction times.

The ^1H NMR spectra of ligands **a** and **d** showed two broad signals assigned to the N*H*$_2$ group, *ca.* δ7.20 and δ6.40, the higher frequency resonance is attributable to the formation of a hydrogen bond between this group and the imine nitrogen atom which restricts the rotation of the $\mathbf{NH_2}$ group about the $C(=S)\mathbf{NH_2}$ bond axis. In the case of ligands **b**, **c**, **e** and **f** only one broad signal *ca.* δ7.3 was detected and assigned to the N*H*Me or the N*H*Et resonances. The aromatic region showed resonances in accordance with 4H spin systems, AA′XX′ **a**–**c**, and ABCD **d**–**f**. Thus, for **a**–**c** two apparent doublets *ca.* δ7.5 and δ7.2 were assigned to H2/H6 and H3/H5, respectively; and for **d**–**f** a doublet of doublets *ca.* δ7.6 and a multiplet *ca.* δ7.3 were assigned to H6 and to H3/H4/H5, also respectively. A singlet *ca.* δ8.0 was assigned to the *H*C=N resonance in each case. The IR spectra showed broad ν(N–H) bands due to the NH groups *ca.* 3200–3150 cm^{-1} [16]. Distinctive ν(C=N) and ν(C=S) stretches appeared in the ranges 1608–1593 and 829–801 cm^{-1}, respectively [17].

Reaction of **a**–**f** with [*cis*-$PtMe_2$(cod)] in refluxing n-octane gave the cyclometallated complexes $[Pt\{(4\text{-}MeC_6H_3)C(H)=NN=C(S)NHR^2\}]_4$, (**1a**, R = H; **1b**, R = Me; **1c**, R = Et) and $[Pt\{(2\text{-}MeC_6H_3)C(H)=NN=C(S)NHR^2\}]_4$, (**1d**, R = H; **1e**, R = Me; **1f**, R = Et), respectively, and as orange air-stable solids, with the ligand in the *Z* configuration, which were fully characterized (preparative details, characterizing microanalytical, mass spectra, IR and ^1H NMR data are in Section 4). The elemental analyses were consistent with the proposed formulations, but the FAB mass spectra only showed peaks at low values of *m*/*z*, probably due to a fast fragmentation of the compounds. Nevertheless, the electrospray mass spectra showed the corresponding peaks assigned to the molecular ion, [M$^+$], after consideration of the platinum isotopes, in accordance with the tetrameric structure $[Pt(L\text{-}2H)]_4$ (L-2H: thiosemicarbazone ligand after C–H activation and NH deprotonation) [19]. A similar trend has been observed by us [13,12a] and others [5,18] for other thiosemicarbazone Pd(II) and Pt(II) cyclometallated compounds.

The IR data were in agreement with deprotonation of the ligand at the hydrazynic nitrogen on complex formation [18,19], and also showed the ν(C=N) band shifted to lower wavenumbers [19a,20], contrary to the trend for other thiosemicarbazone complexes were



Scheme 1. (i) *cis*-[$PtMe_2$(cod)], *n*-octane; (ii) PPh_3 (1:4), $CHCl_3$; (iii) $Ph_2(CH_2)_nPPh_2$ (*n* = 2, 3, 4) (1:2), $CHCl_3$; (iv) $Ph_2PR^3PPh_2$ ($R_3 = CH_2$, $C=CH_2$), (1:4), $CHCl_3$; (v) $[W(CO)_5(Ph_2PCH_2PPh_2)]$, $CHCl_3$; (vi) $[W(CO)_5(THF)]$, $CHCl_3$.