

Preliminary communication

Transmetallation of a binuclear complex of nickel(0). Synthesis and structure of $[\text{NiAu}(\text{CNMe})_2(\text{dppm})_2]\text{Cl}$

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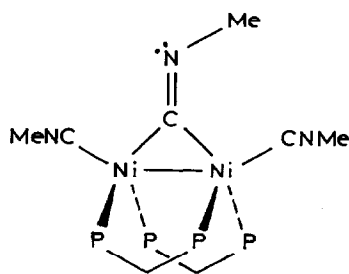
Abstract

The metallation of $\text{Ni}_2(\mu\text{-CNMe})(\text{CNMe})_2(\text{dppm})_2$ (**1**) ($\text{dppm} = \text{PPh}_2\text{CH}_2\text{PPh}_2$) with $(\text{PPh}_3)\text{Au}(\text{Cl})$ affords the transmetallation product, $[\text{NiAu}(\text{CNMe})_2(\text{dppm})_2]\text{Cl}$ (**2**) in 49% yield. The ^{31}P NMR spectrum of **1** is an $\text{AA}'\text{BB}'$ spin system centered at δ 39.2 ppm. An X-ray structural study of the title compound was undertaken. Complex **2** crystallizes in the monoclinic space group Pn with a 12.992(1) Å, b 11.760(1) Å, c 17.579(5) Å, β 109.36(2)°, V 2534(1) Å³, and $Z = 2$. The structure was refined to convergence leading to R and R_w of 0.020 and 0.025, respectively, for 3062 observations in the range $4^\circ < 2\theta < 45^\circ$ with $I > 3.0 \sigma(I)$ and Mo-K_α radiation. The Ni–Au separation is 3.0146(9) Å, suggesting there is not a significant Ni–Au interaction. The complex exhibits a *cis-trans* arrangement of the bridging dppm diphosphine ligands with essentially tetrahedral NiP_2L_2 ($\text{L} = \text{CNMe}$) and linear AuP_2 centers.

Heterobimetallic complexes are of interest for their potential to exhibit cooperative reactivities and unusual chemical and physical properties arising from the alloying of different metals. Shaw and co-workers have been particularly active in preparing homo- and hetero-bimetallic compounds bridged by bis(diphenylphosphino)methane (dppm), using a strategy based on metallation [1,2] and transmetalation [3] of binuclear frameworks. The binuclear complex of nickel(0), $\text{Ni}_2(\mu\text{-CNMe})(\text{CNMe})_2(\text{dppm})_2$ (**1**), recently prepared in our laboratories, possesses a μ -isocyanide ligand with N-atom Lewis basicity exceeding that of ammonia [4]. Complex **1** can be protonated or alkylated under very mild conditions to afford

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(1)

bridging alkylamino- or dialkylamino-carbyne species [4]. The N-atom basicity of **1** also plays an important role in the activation of CO₂ and metathesis of C≡N and C≡O triple bonds [4b,c]. We have therefore undertaken a study of the metallation of **1** via the reactive μ -isocyanide N-atom. The reaction of **1** with [Pd(CNMe)₄][PF₆]₂ was found to give the metallated linear heterotrinnuclear complex [Ni₂Pd(CNMe)₆-(dppm)₂][PF₆]₂ [5]. We now report our study of the reactivity of **1** with (PPh₃)Au(Cl) which affords the transmetallated heterobinuclear complex [NiAu(CNMe)₂-(dppm)₂Cl] (**2**).

Treatment of **1** in THF with (PPh₃)Au(Cl) at room temperature afforded **2** as an orange precipitate [6*]. The product **2** has been characterized by microanalysis, IR, and ¹H and ³¹P NMR spectroscopy [6*]. The ³¹P NMR spectrum of **2** is an AA'BB' spin system centered at δ 39.2, characteristic of an asymmetrically coordinated dppm complex. Both ¹H NMR and ³¹P NMR spectra also indicate that PPh₃ from the starting (PPh₃)Au(Cl) is not contained in the product, **2**. The spectroscopic and analytical data suggest the formulation [NiAu(CNMe)₂(dppm)₂]Cl. A rather similar heterobimetallic compound, [PtAu(CN)₂(dppm)₂]Cl, has been prepared by the reaction of Pt(CN)₂(dppm)₂ with (PPh₃)Au(Cl) [2c]. The structure of **2** was determined by X-ray diffraction [7*] and is presented in Fig. 1. A skeletal view of the molecular cation is presented in Fig. 2. The complex exhibits a *cis-trans* arrangement of the bridging diphosphine ligands, P(11)–Ni–P(12) (120.81(8)°) and P(21)–Au–P(22) (167.54(9)°); and a Ni–Au separation of 3.0146(9) Å, suggesting no significant Ni–Au interaction [8*]. The coordination geometries about the metal centers may be best described as pseudo-tetrahedral about Ni with bond angles ranging from 98.0(2)° to 120.81(8)°, and essentially linear about Au. Similar *cis-trans* dppm frameworks have been observed in homobinuclear nickel complexes Ni₂(μ -CO)(CO)(CNMe)(dppm)₂ [4c] and Ni₂(μ -CNMe)(CNMe)₂(dppm)₂²⁺ [4b]. Owing to the rapidity of the formation of **2**, it has not been possible to determine the role of the μ -isocyanide ligand of **1** in the reaction with (PPh₃)Au(Cl). However, treatment of the (dimethylamino)carbyne compound, [Ni₂(μ -CNMe₂)(CNMe)₂-(dppm)₂]I, prepared by alkylation of **1** with MeI [4a], with (PPh₃)Au(Cl) did not afford the transmetallation product **2**. This result suggests that an initial interaction of the μ -CNMe nitrogen atom lone pair with the gold fragment Au(PPh₃)⁺ may be a key step in the transmetallation of **1**. Our ongoing studies of the metallation and transmetallation chemistry of **1** will be continued along these lines.

* This and other references marked with asterisks indicate notes occurring in the list of references.

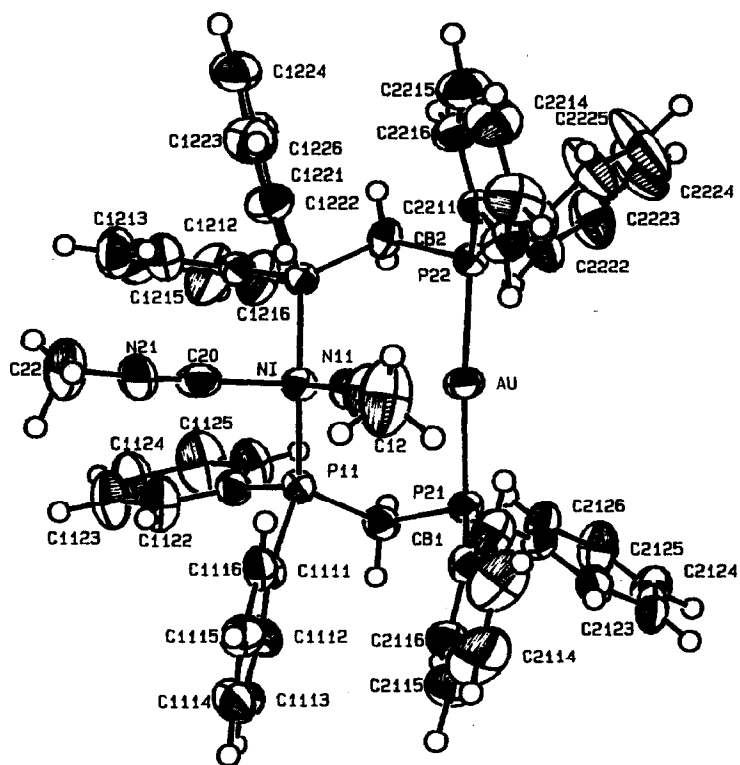


Fig. 1. ORTEP drawing of $(\text{CNMe})_2\text{Ni}(\text{dppm})_2\text{Au}^+$, 2, with 50% probability thermal ellipsoids.

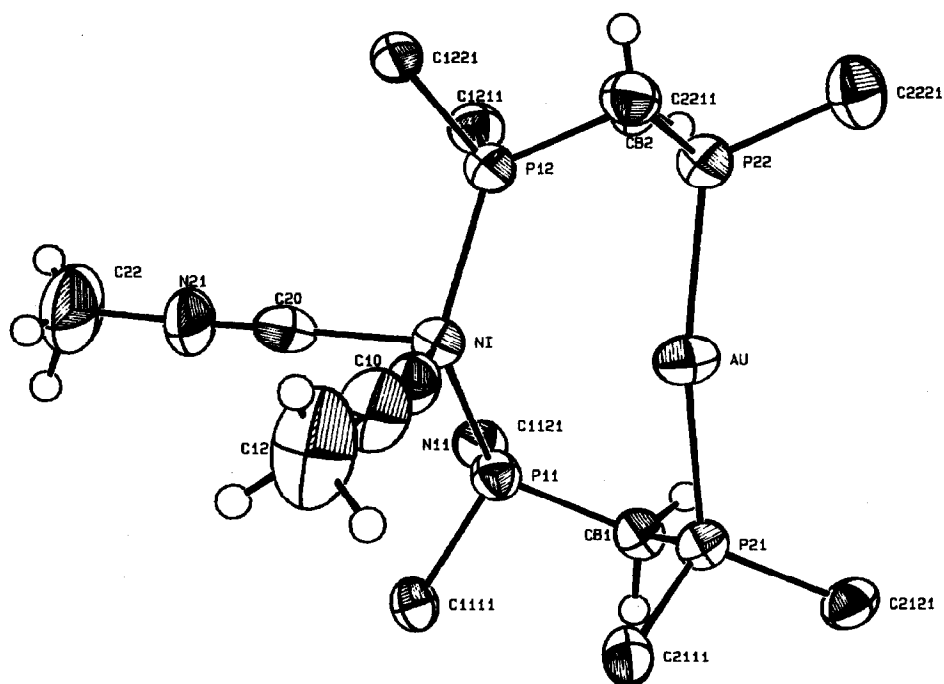


Fig. 2. Skeletal view of 2.

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- 6 To a solution of $\text{Ni}_2(\mu\text{-CNMe})(\text{CNMe})_2(\text{dppm})_2$ (181 mg, 0.179 mmol) in 30 ml THF was added $(\text{PPh}_3)\text{Au}(\text{Cl})$ (95 mg, 0.19 mmol). After the orange solution was stirred for 30 min, an orange solid was precipitated. The IR spectrum of the solution shows $\nu(\text{CN})$ 2066 cm^{-1} , corresponding to $\text{Ni}(\text{CNMe})_4$. The orange solid, **2**, was filtered, washed with hexane and dried under vacuum: total yield 0.1 g (49%); IR(KBr): $\nu(\text{CN})$ 2126, 2091 cm^{-1} ; UV-Vis (CH_3CN , λ_{max} , nm (ϵ)) 389 (8960), 303 (14200); ^1H NMR (CD_3CN , 25 °C): δ 7.0–7.8 (m, 40 H), 4.25 (m, 4 H), 2.34 (s, br, 6H); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN , 25 °C): δ 39.2 (AA'BB'), estimated δ_{A} , δ_{B} by simulation 40.23, 37.99, $^2J_{\text{AB}} + ^4J_{\text{AB}} = 140$ Hz. Anal. Found: C, 56.33; H, 4.29; N, 2.39. $\text{C}_{54}\text{H}_{50}\text{AuClN}_2\text{NiP}_4$ calcd.; C, 56.79; H, 4.41; N, 2.45%.
- 7 Single crystals of **2*** were obtained by slow diffusion of ether into a CH_3CN solution of the sample. Crystal data for **2**: $\text{C}_{54}\text{H}_{50}\text{AuClN}_2\text{NiP}_4$, F.W. = 1142.0, monoclinic space group Pn , a 12.992(1), b 11.760(1), c 17.579(5) Å, β = 109.36(2)°, V = 2534(1) Å³, Z = 2, d_{calcd} = 1.497 $\text{g}\cdot\text{cm}^{-3}$. The structure was solved by MULTAN-least squares-Fourier methods and was refined to R and R_w of 0.020 and 0.025, respectively, for 568 variables and 3062 unique observations with $I > 3.0\sigma(I)$ with Mo- K_α (λ 0.71073 Å) radiation. Data were corrected for absorption empirically.
- 8 The sum of tetrahedral covalent radii of Ni (1.21 Å) and Au (1.50 Å) is 2.71 Å: B.T. Kilbourn, H.M. Powell, *J. Chem. Soc. A*, (1970) 1688; M.L. Huggins, *Phys. Rev.*, 28 (1926) 1086; L. Pauling, M.L. Huggins, *Z. Krist.*, 87 (1934) 205.

* Supplementary Material Available: Tables of crystal data and conditions for data collection, positional parameters, general temperature factor expressions, bond distances and angles, and torsion angles (22 pages) as well as observed and calculated structure factors (22 pages).