Platinum Clusters

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Monomeric Chini-Type Triplatinum Clusters Featuring Dianionic and Radical-Anionic π^* -Systems

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Dedicated to Professor Christopher C. Cummins on the occasion of his 50th birthday

Abstract: Owing to their unique topologies and abilities to selfassemble into a variety of extended and aggregated structures, the binary platinum carbonyl clusters $[Pt_3(CO)_6]_n^{2-}$ ("Chini clusters") continue to draw significant interest. Herein, we report the isolation and structural characterization of the trinuclear electron-transfer series $[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]^{n-}$ (n=0, 1, 2), which represents a unique set of monomeric Pt_3 clusters supported by π -acidic ligands. Spectroscopic, computational, and synthetic investigations demonstrate that the highest-occupied molecular orbitals of the mono- and dianionic clusters consist of a combined π^* -framework of the CO and $CNAr^{Dipp2}$ ligands, with negligible Pt character. Accordingly, this study provides precedent for an ensemble of carbonyl and isocyanide ligands to function in a redox noninnocent manner.

Highly reduced carbonyl metalates have long interested organometallic chemists owing to their ability to place a relatively electropositive transition-metal center in a formally negative oxidation state.^[1,2] This phenomenon is made possible in large part due to the strong π -acidic properties of the carbonyl ligand and has allowed for the isolation of many mono- and multi-nuclear binary carbonyl metalates from most members of the transition series.^[3-6] With regard to topology and electronic structure, one of the most intriguing classes of such complexes are the so-called "Chini clusters," $[Pt_3(CO)_6]_n^{2-.[6-8]}$ In these clusters, *triangulo*-Pt₃ units bearing both terminal and bridging carbonyl ligands stack one on top of the other along a common C_3 axis to form columnar structures bearing an overall doubly anionic charge. The higher nuclearity oligomers (n = 5-8) can self-assemble into continuous chains, with the dimensionality of long-range ordering being highly dependent upon the identity of the charge-balancing cations.^[9-11] Many of the higher ordered structures display remarkable conductive properties, leading to interest in their use as tunable conductive materials based off of a molecular platform.^[12,13] As such, a furthered understanding of the electronic structure and reactivity profiles available to these clusters continues to be of importance.^[14]

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While the oligometric members of $[Pt_3(CO)_6]_n^{2-}$ with n =2-8 have all been isolated and structurally characterized,^[7-11,15] the parent species $[Pt_3(CO)_6]^{2-}$ (n=1) has eluded complete characterization. Although reportedly synthesized in situ via reduction of $[Pt_3(CO)_6]_2^{2-}$ with Na/K alloy, it could not be crystallized or precipitated from solution, with characterization relying solely upon IR and atomic absorption spectroscopies. Interestingly, although several mixed carbonyl/phosphine clusters of the type $Pt_3(\mu-CO)_3(PR_3)_3$ have been long-known,^[16-20] their reduction to the corresponding platinates has not been reported, potentially implying that the weak π -accepting properties of triorganophosphines are insufficient to stabilize the presence of two negative charge equivalents.^[21] Given our success in isolating isocyano analogues to classical carbonyl metalates using sterically encumbering *m*-terphenyl isocyanides, [22-25] we report herein the synthesis and structural characterization of K₂[Pt₃(µ- $CO_{3}(CNAr^{Dipp2})_{3}$ (Ar^{Dipp2} = 2,6-(2,6-(*i*-Pr)_{2}C_{6}H_{3})_{2}C_{6}H_{3}), as well as the open-shell monoanion $K[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]$. These anionic clusters serve as isolobal mimics to $[Pt_3(CO)_6]^{2-1}$ as well as putative [Pt₃(CO)₆]^{.-}, with the highest occupied orbital shown to be primarily located on the ligand π^* framework. Occupation of this highly delocalized π -symmetric orbital results in the aggregate set of isocyanide and carbonyl ligands functioning in a redox non-innocent fashion akin to multidentate redox active ligands.^[26-28]

Exposure of a diethyl ether solution of two-coordinate Pt(CNAr^{Dipp2})₂^[29,30] to 1 atm CO gas results in displacement of one isocyanide ligand and aggregation to afford the trinuclear cluster $Pt_3(\mu$ -CO)₃(CNAr^{Dipp2})₃ (1, Scheme 1). Despite the presence of excess CO, further CO-for-isocyanide substitution is not observed even upon stirring for several days. Crystallographic characterization of 1 (Figure 1A) reveals an equilateral triangulo-Pt₃ core with Pt-Pt distances (mean = 2.6496(2) Å) similar to those seen for $Pt_3(\mu$ -CO)₃(PR₃)₃.^[16-20] Trinuclear **1** adopts nearly ideal D_{3h} site symmetry, with the Pt-CO and Pt-CNR bond vectors all essentially coincident with the Pt₃ plane (maximum torsion $angle = 8.56^{\circ}$). In accordance with its high symmetry in the solid state, the solution FTIR spectrum of **1** displays only a single $v(C \equiv N)$ and ν (C=O) mode (2118 and 1834 cm⁻¹, respectively; E' symmetric in the D_{3h} point group).

Remarkably, cyclic voltammetry of **1** in THF (Figure S3.1 in the Supporting Information) shows the presence of two reversible reduction events centered at -1.95 V ($\Delta E_p = 86 \text{ mV}$) and -2.60 V ($\Delta E_p = 81 \text{ mV}$) versus Fc (Fc = [(η^5 -C₅H₅)₂Fe]), suggesting the accessibility of the anionic clusters [Pt₃(μ -CO)₃(CNAr^{Dipp2})₃]ⁿ⁻ (n = 1, 2). Chemical reduction of



Scheme 1. Synthesis of clusters 1, K[1], and $K_2[1]$.

1 in benzene solution using an excess of KC8 results in smooth formation of a deep purple diamagnetic product as assayed by ¹H and ¹³C{¹H} NMR spectroscopy and proposed to be $K_2[Pt_3(\mu CO_{3}(CNAr^{Dipp2})_{3}]$ (K₂[1]; Scheme 1). Retention of the *triangulo*-Pt₃(μ -CO)₃-(CNR)₃ motif is suggested by peaks at $\delta = 242.2$ and $\delta = 194.5$ ppm in the ¹³C-^{{1}H} NMR spectrum corresponding to bridging carbonyl and terminal isocyanide ligands, respectively. This new species gives rise to a ¹⁹⁵Pt NMR signal at $\delta =$ -4271 ppm, which is strikingly similar to that of $\mathbf{1}$ ($\delta = -4319$ ppm) given the wide chemical shift range inherent in 195Pt NMR.^[31] FTIR spectra in C₆D₆ show a single ν (C=O) band at 1722 cm⁻¹, as well as broad $\nu(C \equiv N)$ stretching modes centered at 2043 and 1985 cm⁻¹. These bands are shifted to significantly lower energies relative to 1 and can be compared with the bridging and terminal $\nu(CO)$ modes reported for in situ gener-



Figure 1. Molecular structures of 1 (A), $[K_2(DME)_3]$ [1] (B) and $[K(THF)_4]$ [1] (C). Some *iso*-propyl groups have been removed for clarity. D) Experimental (black) and simulated (gray-dashed) X-band powder EPR spectrum of $K(THF)_4$ [1] recorded at 294 K.

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ated [Pt₃(CO)₆]²⁻ (1945, 1740 cm⁻¹, THF).^[8]

Structure determination on single crystals of $K_2[1]$ grown from DME/*n*-hexane at -35 °C confirmed the identity of this species to be the dianion $K_2(DME)_3[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]$ ($K_2(DME)_3[1]$, Figure 1B). Each Pt_3 unit exists as a discreet entity and no oligomerization to higher nuclearity, stacked structures is observed. Most notably, despite the introduction of two negative charge equivalents, the structural features of the $[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]$ core in $K_2(DME)_3[1]$ are essentially unchanged relative to 1. The Pt–C bond vectors remain nearly coincident with the Pt₃ plane, with only very minor perturbations of the Pt–Pt, Pt–C_{CNR}, and Pt–C_{CO} distances apparent (Table 1). The two potassium counterions sit

Table 1: Selected bond lengths from the solid-state structures of complexes 1, $K(THF)_4[1]$, and $K_2(DME)_3[1]$.

Complex	Mean <i>d</i> (Pt-Pt) [Å]	Mean <i>d</i> (Pt-C _{CNR}) [Å]	Mean <i>d</i> (Pt-C _{co}) [Å]
1	2.6496(2)	1.917(3)	2.062(2)
K(THF)₄[1]	2.6448(3)	1.924(6)	2.047(4)
K ₂ (DME) ₃ [1]	2.6359(2)	1.896(4)	2.044(3)

directly over the centroid on either face of the Pt_3 triangle and are chelated by one or two molecules of DME.

In contrast to Chini's $[Pt_3(CO)_6]^{2-,[8]} K_2[1]$ exhibits remarkable kinetic stability. As a solid, it can be stored for weeks in a glovebox freezer at -35 °C without change, while $[D_6]$ benzene solutions of $K_2[1]$ at 25 °C undergo decomposition over the course of several weeks to give free CNAr^{Dipp2} as the sole isocyanide-containing species according to ¹H NMR spectroscopy. This kinetic stability results in an exceedingly simple synthetic method whereby analytical quality $K_2[1]$ can be obtained in excellent yields (99%) via simple lyophilization of the benzene solvent after filtration of the reaction mixture.

While Chini clusters of many nuclearities have been isolated, a common feature among all of them is an overall charge of 2-. Their reactions with oxidizing agents have been proposed to proceed via single-electron transfer to transiently form $[Pt_3(CO)_6]_n$, followed by dimerization and further aggregation to yield $[Pt_3(CO)_6]_{2n}^{2-}$ stacked clusters.^[32] However, such monoradical species have not been observed to date during the course of these oxidations. The apparent resistance of $K_2[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]$ ($K_2[1]$) toward aggregation, as well as the clean electrochemical data for 1, suggested the potential accessibility of the open-shell monoanion [Pt₃(µ-CO)₃(CNAr^{Dipp2})₃]. Accordingly, simple comproportionation of 1 and $K_2[1]$ in $[D_8]THF$ (Scheme 1) produces a dark green solution, which gives rise to only broad ¹H NMR signals indicative of the presence of a paramagnetic species ($\mu_{eff} = 1.7(2) \mu_B$, Evans method). Analysis by FTIR spectroscopy shows ν (C=O) (1775 cm⁻¹) and ν (C=N) (2061, 2022 cm⁻¹) bands intermediate in energy with respect to those of 1 and $K_2[1]$. Storage of this solution at -35 °C yields black crystals of $K(THF)_4[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]$ $(K(THF)_{4}[1])$ as determined by X-ray diffraction (Figure 1 C). As noted for $K_2(DME)_3[1]$, the anionic fragment in K(THF)₄[1] is essentially isostructural to that of neutral 1 (Table 1). The coordination geometry about each platinum center remains almost perfectly planar, while the Pt–Pt, Pt– C_{CNR} , and Pt– C_{CO} bond lengths are basically unchanged from those in 1 and K₂(DME)₃[1] (Table 1). The room temperature solid-state EPR spectrum of K(THF)₄[1] displays axial symmetry, with $g_{\perp} = 2.020$ and $g_{\parallel} = 1.974$ (Figure 1D). The small degree of g anisotropy and the minimal deviation of these values from 2.002 (g of a free electron) differ from EPR spectra typically seen for Pt-based S = 1/2 metalloradicals.^[33-35] However, they are very much in accord with spectra exhibited by systems containing closed-shell platinum centers bound to radical ligands.^[36,37] Noticeably, no coupling to the ¹⁹⁵Pt nucleus (I = 1/2, 33.8% abundant) is resolved, suggesting that minimal spin density resides at the Pt₃ core.

Density Functional Theory (DFT) studies were undertaken in order to interrogate the electronic structure of the clusters $[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]^{n-}$ (n=0, 1, 2). The optimized geometries of the truncated models $[Pt_3(\mu-CO)_3-(CNAr^{Ph2})_3]^{n-}$ ($[\mathbf{1*}]^{n-}$, n=0, 1, 2) satisfactorily reproduce the important metrical parameters of the corresponding structurally characterized triplatinum clusters $\mathbf{1}$, $K(THF)_4[\mathbf{1}]$ and $K_2(DME)_3[\mathbf{1}]$ (Figures S4.1–3 and Tables S4.1–3). Remarkably, the calculated HOMO of $[\mathbf{1*}]^{2-}$ (Figure 2A)



Figure 2. DFT Calculated HOMOs of $[1^*]^{2^-}$ (A), $[Pt_3(CO)_6)]^{2^-}$ (B), and $[Pt_3(\mu$ -CO)_3(PMe_3)_3]^{2^-} (C). BP86/def2-TZVP/ZORA.

and SOMO of $[1^*]^-$ consist of the in-phase combination of the out-of-plane π^* orbitals of the carbonyl and isocyanide ligands $(a_2^{"} \text{ in } D_{3h} \text{ symmetry})$ with only a modest contribution from Pt-based orbitals (20.5% for $[1^*]^{2-}$ HOMO; 25.7% for $[1^*]^-$ SOMO).^[38] The primarily ligand-based parentage of this orbital is in accord with the minimal shortening of the Pt–C bond distances upon reduction of 1 (Table 1), despite the sizeable shift of the IR ν (C=O) and ν (C=N) bands to lower energies, which are usually attributable to increased metal-to-ligand π -backdonation. It is also consistent with semi-empirical extended Hückel calculations on $[Pt_3(CO)_6]^{2-}$, which predict a HOMO that is primarily CO π^* in charac-



ter.^[39-41] Indeed, DFT calculations on [Pt₃(CO)₆]²⁻ yield a HOMO that is entirely analogous to that of $[1^*]^{2-}$, namely the $a_2^{"}$ combination of bridging and terminal CO out-of-plane π^* orbitals (Figure 2B). This confirms that $K_2[1]$ indeed functions as an isolobal analogue of $[Pt_3(CO)_6]^{2-}$, while K[1] is isolobal with the monoanion $[Pt_3(CO)_6]^{-}$, a putative fleeting intermediate in the oxidation of $[Pt_3(CO)_6]^{2-}$ to $[Pt_3(CO)_6]_2^{2-}$. The all- π -acid ligand sets employed in K₂[1] and [Pt₃(CO)₆]²⁻ can be contrasted with the hypothetical dianions of the phosphine-substituted triplatinum clusters $Pt_3(\mu-CO)_3$ - $(PR_3)_3$.^[16-20] DFT calculations for $[Pt_3(\mu-CO)_3(PMe_3)_3]^{2-}$ illustrate that the primarily σ -donating nature of the trimethylphosphine ligands precludes delocalization of electron density onto the terminal ligands in the cluster. For this complex, the HOMO is again $a_2^{\prime\prime}$ -symmetric, but consists primarily of the out-of-plane π^* orbitals of the bridging carbonyl ligands (Figure 2 C). The relative localization of electron density onto the bridging ligands in $[Pt_3(\mu-CO)_3(PMe_3)_3]^{2-}$, along with the strongly o-donating nature of the phosphine ligands, likely renders the reduction of $Pt_3(\mu$ -CO)₃(PR₃)₃ to the corresponding dianion more difficult than the reduction of 1 to $K_2[1]$, and serves to highlight the central role played by the all- π -acid ligand sets of $K_2[1]$ and $[Pt_3(CO)_6]^{2-}$ in stabilizing the negative charge equivalents.

Interestingly, the modest contribution of platinum-based atomic orbitals to the a_2 "-symmetric HOMO of $[1^*]^{2^-}$ is mostly $6p_z$ in parentage, while the molecular orbital contains only 0.8% 5 d character. Similarly small 5 d contributions are apparent in the SOMO of $[1^*]^-$ (1.3% 5 d) and the HOMO of $[Pt_3(CO)_6]^{2^-}$ (1.4% 5 d), an effect we believe can be traced to the intratriangular Pt–Pt bonding interactions.^[42] Indeed, the only symmetry-adapted linear combination of Pt 5d orbitals for the [Pt(μ -CO)₃L₃] (L=CO, CNR) fragment with a_2'' symmetry (Figure S4.6-8) has significant Pt-Pt bonding character, which serves to significantly lower it in energy. Importantly, the resulting energy gap between these d orbitals and the $a_2^{\prime\prime}$ -symmetric π^* manifold is substantial (4.40– 4.54 eV), which precludes significant orbital mixing. Remarkably, owing to the primarily ligand-based nature of the a_2'' HOMO/SOMO found for $[1^*]^{2-}$ and $[1^*]^{-}$, it can be noted that population of this orbital in $K_2[1]$ and K[1] results in the CO/CNAr^{Dipp2} ligand set acting in a formally redox noninnocent fashion. Distinct from these ligands merely functioning as π -acids, the successive reduction on going from 1 to $K(THF)_4[1]$ and $K_2[1]$ yields clusters best described as containing a $(Pt_3)^0$ core supported by a ligand set that, as an aggregate, bears a singly- or doubly-reduced π^* -manifold. In essence, combining the out-of-plane π^* orbitals of all six ligands in-phase renders them accessible in energy, allowing the $a_2^{\prime\prime}$ orbital to function as an electron reservoir reminiscent of multidentate redox non-innocent ligand systems bearing extended π -systems.^[26]

The robust and highly-reduced nature of $K_2[Pt_3(\mu-CO)_3(CNAr^{Dipp2})_3]$ ($K_2[1]$) allows it to undergo well-defined reactivity with main-group and transition-metal electrophiles (Scheme 2). Addition of a benzene solution of Ph₃SnCl or Et₃SiCl to $K_2[1]$ proceeds with elimination of KCl and formation of the diamagnetic triplatinum clusters K[Pt_3(μ_3 -SnPh_3)(μ -CO)₃(CNAr^{Dipp2})₃] (**2**, Figure 3A) or K[Pt_3(SiEt_3)-(μ -CO)₃(CNAr^{Dipp2})₃] (**3**, Figure 3B) as determined by X-ray diffraction. In **2**, the triphenylstannyl ligand is bound in a μ_3 fashion, a binding mode that is unprecedented for triorga-



Scheme 2. Reactivity of K₂[1] with electrophiles.

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Figure 3. Molecular structure of A) $K[Pt_3(\mu_3-SnPh_3)(\mu-CO)_3(CNAr^{Dipp2})_3]$ (2), B) $K(Et_2O)[Pt_3(SiEt_3)(\mu-CO)_3(CNAr^{Dipp2})_3]$ (3), C) $K(Et_2O)_2[Pt_3(\mu_3-AuPPh_3)(\mu-CO)_3(CNAr^{Dipp2})_3]$ (4), and D) $Pt_3(\mu_3-AuPPh_3)_2(\mu-CO)_3(CNAr^{Dipp2})_3$ (5). Some *i*Pr groups have been removed for clarity.

nostannyl ligands.^[43] Contrastingly, the triethylsilyl ligand in 3 is terminally bound to a single Pt center, with the Pt-Si bond vector being nearly orthogonal to the Pt₃ plane. The isocyanide bound to the silyl-ligated platinum center bends significantly out of the plane toward the opposite face of the cluster. However, despite the asymmetry evident in the solidstate structure of 3, only a single sharp set of -Ar^{Dipp2} resonances are detected by ¹H NMR spectroscopy at 20°C, indicating that exchange of the silvl ligand between the three Pt centers is fast on the NMR timescale. Dianionic K₂[1] also reacts with one or two equivalents of AuCl(PPh₃), providing dark blue $K(Et_2O)_2[Pt_3(\mu_3-AuPPh_3)(\mu-CO)_3(CNAr^{Dipp2})_3]$ (4, or forest green $Pt_3(\mu_3-AuPPh_3)_2(\mu-$ Figure 3C) CO₃(CNAr^{Dipp2})₃ (5, Figure 3D). In both clusters, the -AuPPh₃ fragments symmetrically bridge the three Pt centers affording a Pt_3Au tetrahedron (4) or a Pt_3Au_2 trigonal bipyramid (5). While reminiscent of the formation of $[Pt_3(\mu_3-AuPCy_3)(\mu-CO)_3(PCy_3)_3]^+$, which is produced by capping the corresponding neutral Pt₃ cluster with a $[AuPCy_3]^+$ fragment,^[44] it should be noted that the two additional valence electrons possessed by $K_2[1]$ compared to $Pt_3(\mu$ -CO)₃(PCy₃)₃ allows for the isolation of an anionic Pt/Au cluster, of which only one other structurally characterized example is known.^[45] These extra electrons also allow for the formation of 5 via addition of a second equivalent of $[AuPPh_3]^+$, a transformation which is not accessible to $[Pt_3(\mu_3-AuPCy_3) (\mu$ -CO)₃(PCy₃)₃]^{+[46]} and has not been reported for any phosphine-substituted $Pt_3(\mu-CO)_3(PR_3)_3$ cluster. Accordingly, these reactions leading to the formation of complexes 2-5 demonstrate that while e^- equivalents are housed in the ligand-based π^* manifold of K₂[1], electrophilic functionalization can proceed at the platinum centers of the *triangulo*-Pt₃ core.

In conclusion, the kinetic stabilization afforded by encumbering m-terphenyl isocyanides, in concert with their isolobal relationship to CO, allows for the isolation of a robust analogue to Chini's [Pt3- $(CO)_6]^{2-}$ dianion. Remarkably, the corresponding monoanion is also isolable and was shown to contain one unpaired electron located primarily on the aggregate ligand π^* system. Importantly, this study provides precedent for a set of isocyanide and carbonyl ligands to act in a redox non-innocent fashion. We are exploring additional reactivity patterns of these Pt₃ clusters that harness this unique electronic structure feature.

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