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Electron-Deficient η^1-Indenyl,η^3-allylpalladium(II) Complexes Stabilized by Fluxional Non-covalent Interactions

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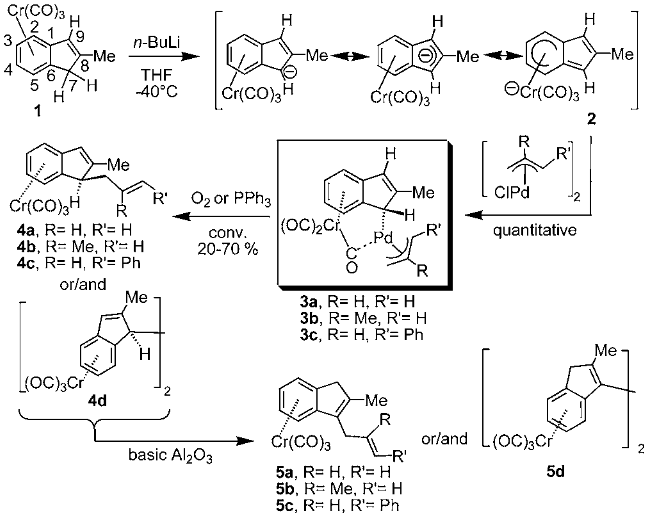
Supporting Information

ABSTRACT: Highly fluxional, solution-persistent, and formally electron-deficient (32e$^-$) binuclear Pd(II)-C(0) complexes of 2-methyl-1*H*-indene were synthesized and structurally characterized by X-ray diffraction analysis. DFT investigations combined with a number of theoretical analyses of the bond framework suggest that the polar intermetallic interaction possesses no major covalent character. Instead of bearing a static metal-metal bond as suggested by structural X-ray diffraction analysis, the complexes display in solution significant fluxionality through haptotropy, i.e., a formal "oscillation" of the Pd(η^3-allyl) moiety between two limiting η^1-indenyl configurations.

Hemilability is an important property of transition metal ligands. It enables, upon appropriate chemical solicitation, the creation of a vacant coordination site and extension of the coordination environment of the considered metal. To some extent, the so-called "indenyl effect" (IndE),[1] which has been documented for a host of metal complexes,[2] can also be considered as a form of *intrinsic hemilability*. IndE is often associated with the unique ability of the indenyl ligand to undergo a "slip-fold" η^5-to-η^3 distortion in d$^{0\text{-}9}$ metal complexes;[3] IndE plays an important role in the reactivity of d-block metals and in stoichiometric reactions as well as in metal-mediated catalytic transformations.[3c,4] Although a wide variety of η-indenyl complexes of group 10 metals have been reported,[5,6] both η^3 and η^1 coordination modes have been depicted as stable and persistent in solution.[7] Now, a new methodology for synthesizing electron-unsaturated and fluxional indenylpalladium(II) complexes is proposed. It exemplifies the directing and stabilizing virtues of non-covalent interactions like Coulombic attraction and electron correlation between two metal centers in a prototypical ambident indenyl ligand that contains a benzo ring-bound Cr(CO)$_3$ fragment capable of establishing stabilizing interactions with a vicinal syn-facial electron-deficient Pd(II) center covalently bonded to the five-membered ring. The synthesis, structural characterization, electronic structure, and dynamic behavior of the new 14-electron (η^3-allyl)Pd(II) complexes containing the ambident tricarbonyl(η^6-indenyl)chromium (Scheme 1) are addressed.

Indene complexes like **1** (Scheme 1) can be readily deprotonated to afford the corresponding anion **2**, the stability of which stems from a major delocalization of charge density all over the complex down to the Cr and O atoms of the Cr(CO)$_3$ moiety best illustrated by the three limiting forms in Scheme 1. The strong charge density imbalance in anions like **2** influences the stereochemical course of reactions with transition metals. It was shown[8,9] that adding chlorido Ir(I) and Rh(I) complexes to the tricarbonyl(η^6-indenyl)chromium anion generally yields the syn-facial heterobimetallic product as a consequence of driving attractive intermetallic and metal/ligand electron correlation as well as dispersion force. Here, treating **2** with a stoichiometric amount of bis[(η^3-allyl)palladium chloride], bis[(η^3-2-methylallyl)palladium chloride], or bis[(η^3-1-phenylallyl)palladium chloride] led after ~1 h to quantitative formation of **3a-c**, according to ^{1}H NMR analyses of the reaction medium. Solutions of **3a,b** in toluene were persistent for few days, allowing isolation and subsequent analytical characterization. Suitable crystals for structural X-ray diffraction analyses were obtained under anaerobic conditions by slowly diffusing solutions containing a majority of toluene into dry *n*-heptane and subsequently handled wet under a cold argon stream to prevent decomposition. Figure 1 displays the ORTEP diagrams of **3a-c**, which reveal that the Pd(II) center is not only η^1-bonded

Scheme 1. Synthesis of Complexes 3a-c Derived from 2-Methyl-1*H*-indene and the Decomposition Pathway



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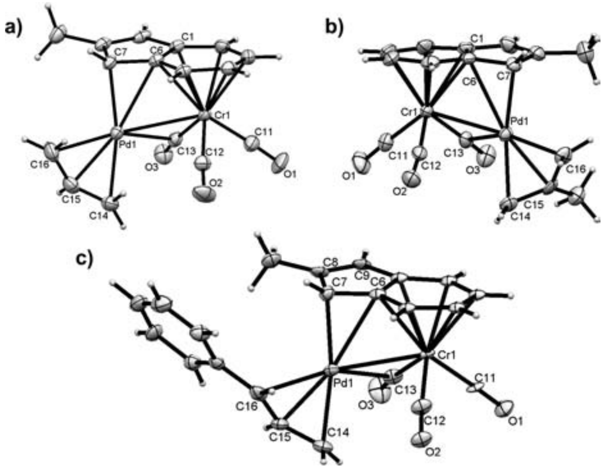

Figure 1. ORTEP diagrams of **3a**-**c** at the 50% level; a molecule of toluene solvent is omitted for clarity in the structure of **3b**. Selected interatomic distances (Å): (a) Cr(1)-Pd(1) 2.7542(6), Cr(1)-C(11) 1.831(4), Cr(1)-C(12) 1.839(4), Cr(1)-C(13) 1.873(4), Pd(1)-C(13) 2.428(4), Pd(1)-C(6) 2.547(3), Pd(1)-C(7) 2.174(4), Pd(1)-C(16) 2.147(4), Pd(1)-C(15) 2.133(4), Pd(1)-C(14) 2.174(4); (b) Cr(1)-Pd(1) 2.7466(6), Cr(1)-C(11) 1.853(4), Cr(1)-C(12) 1.846(4), Cr(1)-C(13) 1.862(4), Pd(1)-C(13) 2.443(4), Pd(1)-C(6) 2.614(3), Pd(1)-C(7) 2.184(3); (c) Cr(1)-Pd(1) 2.7371(16), Cr(1)-C(11) 1.846(9), Cr(1)-C(12) 1.852(10), Cr(1)-C(13) 1.861(10), Pd(1)-C(13) 2.345(10), Pd(1)-C(6) 2.575(9), Pd(1)-C(7) 2.193(9).

to the indenyl's five-membered ring but also apparently engaged in a delocalized interaction with a proximal carbonyl ligand and with the Cr atom. The Pd-Cr distance of ~2.75 Å lies in the range of those reported by Kalinin et al.[10] for two [(η^6:η^1-benzyl)-tricarbonylchromium][(η^3-allyl)palladium] complexes. The C(13)-Pd distance of ~2.44 Å that materializes in the interaction between a CO ligand and the Pd center is slightly shorter than in Kalinin's cases. The slight bending of the related Cr-C(13)-O(3) angle of ~170° and the slightly elongated Cr-C(13) distance, as compared to Cr-C(12), suggests a weak bridging interaction. ATR-FTIR spectra of amorphous powders of **3a**,**b** did not reveal any typical CO stretching mode expected for a bridging CO ligand but rather the expected stretching modes of a *fac*-$L_3Cr(CO)_3$ moiety consisting of a strong narrow band at 1930 cm^{-1} and a strong and broad band centered at 1840 cm^{-1}. Similarly, **3c** displayed CO stretching bands at 1941 (strong), 1864 (strong), and 1821 (strong) cm^{-1}.

Given the possible role of nonlocal interactions (dispersion) in stabilizing bimetallics like **3a**-**c**,[9,11] state-of-the-art DFT-D3[12] methods as well as other dispersion-corrected functionals, e.g., PBE0-dDsC,[13] M06-L, and M06-2X,[14] were considered to address the issues of bonding and electronic structure (cf. Supporting Information (SI) and Table 1). Grimme's DFT-D3 methods with the so-called Becke-Johnson (BJ)[15] damping function, e.g., TPSS[16]-D3(BJ)[12,15] or PBE[17]-D3(BJ),[12,15] and Corminboeuf's density-dependent dispersion-corrected functional PBE0[18]-dDsC[13a] reproduced well the singlet ground-state geometry of **3b**, particularly in the vicinity of the two metal atoms, a critical area where non-covalent interactions obviously dominate. Notably, M06-2X[14] and B3LYP[19] equally produced long and non-realistic interatomic distances for Cr-arene and Pd-allyl bonds. The largest deviation from experiment, i.e., ~0.1 Å, was noticed for the Cr-Pd distance. Therefore, further investigations were carried out with PBE-D3(BJ), TPSS-D3(BJ), or PBE0-dDsC functionals associated with all-electron triple-ζ Slater-type basis sets for all elements within the ZORA[20] formalism. Calculations performed on models of **3a**,**b** confirmed that the η^1 coordination mode of the cyclopentadienylic part of the indenyl ligand to Pd surpassed in stability the η^3 one by ~11 kcal/mol (including zero point energy, ZPE) in the *syn*-facial bimetallic arrangement, where the Cr-Pd distance amounts to ~2.7 Å. The η^3 mode entails a Cr-Pd distance of ~3.1 Å, with an anti-eclipsed conformation of the $Cr(CO)_3$ tripod. Furthermore, the η^1 syn-facial arrangement was more favorable by ~13 kcal/mol (ZPE included) than the antara-facial alternative, which favors η^3 coordination of the indenyl to the Pd(II) center, in good agreement with early conclusions of Nakamura et al. on monometallic indenyl analogues.[21]

Table 1. Selected Interatomic Distances (in Å) in Computed Models of 3b with a Selection of Functionals (ZORA, All-Electron TZP Basis Sets)

method	$d_{\text{Cr-Pd}}$	$\Delta d_{\text{Cr-Pd}}$[a]	$d_{\text{Cr-C(6)}}$	$\Delta d_{\text{Cr-C(6)}}$[a]
expt	2.7466(6)	–	2.274(3)	–
PBE-D3(BJ)	2.738	−0.009	2.275	+0.001
TPSS-D3(BJ)	2.722	−0.025	2.272	−0.002
M06-L	2.788	+0.041	2.252	−0.022
M06-2X	2.839	+0.092	2.306	+0.032
PBE0-dDsC	2.724	−0.023	2.251	−0.023
B3LYP	2.832	+0.085	2.316	+0.041
B3LYP-D3	2.782	+0.035	2.299	+0.024

[a] $\Delta d_x = d_x^{\text{calcd}} - d_x^{\text{exptl}}$.

This energetic bias in favor of the η^1 mode in the syn-facial arrangement was investigated by a comparative energy decomposition analysis[23] with η^1-**3a** and η^3-**3a**, which allowed a detailed dichotomy of the intrinsic interaction energy ΔE_{int} into repulsive (Pauli, ΔE^{Pauli}) and attractive (electrostatic ΔE^{elec}, orbital ΔE^{orb}, and dispersion ΔE^{disp}) interaction energy terms for the interactions of prepared anion **2** with prepared [(η^3-allyl)palladium]$^+$. The preference for the η^1 mode stems from larger orbital and electrostatic interaction energy terms, as suggested by the energy difference $\Delta\Delta E_{1\text{-}3} = \Delta E_{\eta 1} - \Delta E_{\eta 3}$: $\Delta\Delta E_{1\text{-}3}^{\text{orb}} = -10.9$ kcal/mol, $\Delta\Delta E_{1\text{-}3}^{\text{elec}} = -15.1$ kcal/mol, $\Delta\Delta E_{1\text{-}3}^{\text{Pauli}} = +6.8$ kcal/mol, $\Delta\Delta E_{1\text{-}3}^{\text{disp}} = -0.4$ kcal/mol, $\Delta\Delta E_{1\text{-}3}^{\text{int}} = -19.7$ kcal/mol. The larger electrostatic term in η^1-**3a** is associated with a marked polarization of the molecule and an imbalance in the charge density distribution around the Pd (natural charge $q_{\text{NPA}} = +0.598$) and Cr ($q_{\text{NPA}} = -0.815$) atoms. Analysis of the Wiberg bond indices (WBI) outlined the low covalent character of the interaction between the Pd center and the arenechromium-tricarbonyl moiety. In η^1-**3a**, $\text{WBI}_{\text{Pd-Cr}}$, $\text{WBI}_{\text{Pd-C(7)}}$, and $\text{WBI}_{\text{Pd-C(13)}}$ amount to 0.14, 0.26, and 0.20, respectively, and the weak covalent Pd-C(13) interaction does not affect $\text{WBI}_{\text{C(13)-O(3)}}$ (2.01), which is similar to $\text{WBI}_{\text{C(12)-O(2)}}$ (2.07). NOCV-ETS analyses[22] provided a picture of the direction of electron density transfer in the orbital interaction between the closed-shell prepared anionic and cationic fragments, i.e., **2** and [(η^3-allyl)palladium]$^+$, respectively, in η^1-**3a**. Figure 2 displays the density-deformation plots of the first four NOCVs of highest orbital interaction energies. The strongest contribution (Figure 2, −53.3 kcal/mol) corresponds to a transfer of electron density from the Cr and benzylic position toward the allyl ligand π system, the Pd center, and the Pd-C(7) σ bond; this contribution of Cr is complemented with a donation of electron density to the C(7)-Pd σ bond from the Pd center in the representation of lowest energy (−7.4 kcal/mol). The Pd-C(13) σ bond (−15.5 kcal/mol) results from density donation of the two metal centers

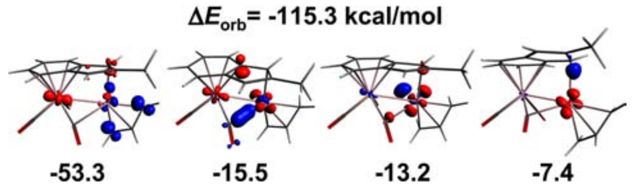

Figure 2. NOCV-ETS[22] $\Delta\rho^{\mathrm{orb}}$ deformation densities computed at the (ZORA[20]) PBE[17][-D3(BJ)]/all-electron TZP level for the interaction between closed-shell prepared fragments **2** and $[(\eta^3\text{-allyl})\mathrm{Pd}]^+$ in η^1-**3a** with the associated orbital interaction energies (kcal/mol) with isosurfaces of 0.01 and 0.005 e/bohr^3 for the plots of highest orbital interaction energy and for the remaining three plots respectively. Blue and red colors are respectively associated with areas of electron density buildup and depletion upon interaction.

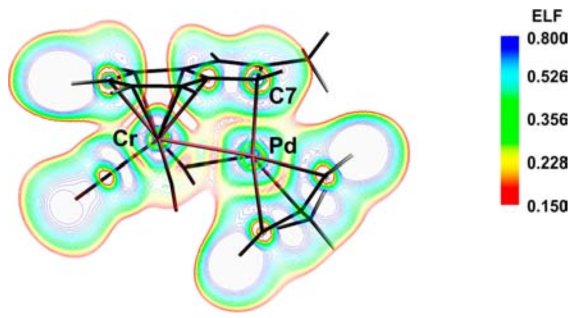

Figure 3. Contour plot of the ELF[24] in **3b** from a (ZORA[20]) PBE0[18] (-dDsC[13a])/all-electron-TZP gas-phase minimum in the plane defined by Cr, Pd, and C(7).

and the arene's π system. As for a possible Cr-Pd interaction (Figure 2, −13.2 kcal/mol), the analysis suggested some density transfer from Pd to the Cr center and toward a volume of space located within the Pd-C(6)-Cr triangle. Analysis of the electron pairing in a geometrically correct model of **3b** (Figure 3) by the electron localization function[24] (ELF) revealed a weak disynaptic domain in the Cr-Pd segment ($0.2 < \mathrm{ELF} < 0.3$) and no sensible disynaptic domain for the Pd-C(13) interaction. In slight contrast, the so-called atom-in-molecules[25] analysis (cf. SI) of the electron density topology revealed no bond critical point (BCP) within or in the vicinity of the Cr-Pd segment. Nonetheless, a BCP displaying features typical of a weak closed-shell interaction was found within the Pd-C(13) segment. In summary, all analyses concurred in establishing the nature of the interaction between the Pd center and the $\mathrm{Cr(CO)_3}$ moiety as mostly non-covalent.

In solution, **3a**-**c** displayed fluxional behavior on the time scale of ^{1}H (600 MHz) and ^{13}C (150 and 125 MHz) NMR spectroscopy. At room temperature, the ^{13}C NMR spectra of the three complexes displayed multiple large signals for the carbonyls of the $\mathrm{Cr(CO)_3}$ moiety: a set of two signals in a 1:2 ratio at ~239 and 235 ppm for **3a**,**b** and a set of three signals in a 1:1:1 ratio at δ 238, 236, and 235 ppm for **3c**. Low-temperature ^{13}C NMR experiments on **3b** further revealed the temperature dependence of the line width and of the apparent intensity ratio of the signals arising from $\mathrm{Cr(CO)_3}$. These symptoms of significant hindrance to rotation operated over the $\mathrm{Cr(CO)_3}$ rotor were accompanied by other signs of fluxionality for the indenyl ^{13}C and ^{1}H signals. The ^{1}H NMR spectra of **3a**,**b** at 298(1) K displayed patterns of apparently symmetric molecules very much in agreement with a putative symmetric η^3-**3a**,**b** static model in which the Pd would be η^3-bound to the indenyl (Figure 4). However, at room temperature, the indenyl protons attached to C(7) and C(9) (Figure 1), i.e., H(7) and H(9), showed up as a single broad singlet in the ^{1}H NMR spectra (600 MHz) that would broaden significantly upon decreasing the temperature to 223(1) K. A full line-shape analysis[26] was undertaken with **3b** assuming that the temperature dependence of the line width of the indenyl-related protons was the result of fluxionality via haptotropy, i.e., reversible migration of the Pd center from C(7) to C(9) in a typical η^1-η^3-η^1 sequence, where the η^3 state is a metastable intermediate (Figure 4). Similar cases of fluxional behavior were evidenced with η^1-bound Cu(I) and Hg(II) indenyl complexes.[27] Convergent DFT calculations of the theoretical ^{1}H NMR spectrum of η^1-**3b** solvated by toluene (COSMO[28] model) at two different levels of theory (ZORA-PBE-D3(BJ)/AE-TZP and ZORA-SAOP[29]/AE-TZP) provided the low-exchange-rate peak separation for uncoupled H(7) and H(9) ($\Delta\delta$ = 0.270 ppm), a key parameter that could not be determined by experiment. The DNMR3 Binsch-Kleier algorithm[30] applied to a set of spectra recorded at 223(1)−273(1) K (cf. SI) provided exchange rates k spanning 2−23.5 kHz. Treatment of the associated Eyring curve produced the enthalpy and entropy of activation, $\Delta H^\ddagger = +6.0(2)$ kcal/mol and $\Delta S^\ddagger = -15.5(9)$ cal/mol·K, which were reasonably approached theoretically (toluene COSMO ZORA-PBE-D3(BJ)/AE-TZP, rigid rotor harmonic oscillator approximation), assuming the $\eta^3 \rightarrow \eta^1$ barrier to be negligible (Figure 4): $\Delta H_c^\ddagger = 9.9$ kcal/mol and $\Delta S_c^\ddagger = -0.7$ cal/mol·K. With **3c**, similar dynamic features were observed in the NMR spectra. However, due to the compound's asymmetry and the near impossibility of measuring the slow exchange ^{1}H NMR spectrum, information from VT NMR data was not sought.

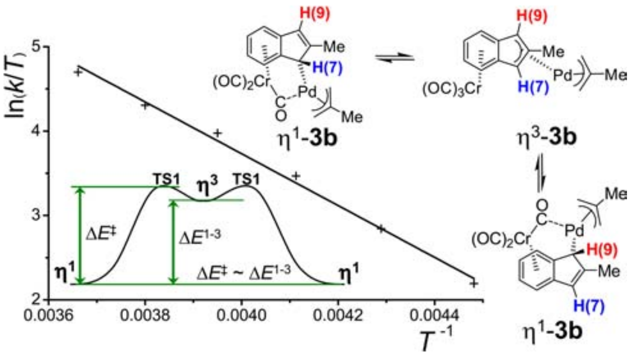

Figure 4. Eyring plot of ln(k/T) vs T^{-1} (K^{-1}) for exchange rate constants (equipopulated mutual exchange, T_2 = 0.5 s) determined from ^{1}H NMR (600 MHz) line-shape analysis of the H(7) and H(9) signals of **3b** between 213(1) and 263(1) K in ~10:1 d_8-toluene/THF.

The possible contribution of the allyl ligand's η^1-η^3 isomerization[31] to the observed fluxionality was ruled out based on theory and experiment. The energies of the related η^1-allyl intermediates were systematically higher than that of the putative η^3 metastable intermediate, whether or not an explicit THF molecule was introduced[31] to promote η^1-η^3 allyl isomerization. ^{1}H NMR signals associated with the terminal $\mathrm{CH_2}$ position of the allyls were insensitive to temperature change in all cases, supporting a passive role of the allyl ligand in the above-mentioned fluxionality. Complexes **3a**-**c** proved to be stable for hours in benzene or toluene solutions under anaerobic conditions. Exposure to air or to a slight excess of $\mathrm{PPh_3}$ led to rapid decomposition by loss of Pd(0), affording a variety of products of heterocoupling between the tricarbonyl(η^6-2-methylindenyl)chromium moiety and the allyl ligand, i.e., **4a**-**c**

(Scheme 1). Compounds **3a**,**b** were generally unstable in the solid state under vacuum, turning swiftly to a black powder containing Pd-black and **4a**,**b**. Compound **3c** was stable in the solid state and displayed sluggish reactivity to air or to PPh$_3$: its decomposition favored indenyl's homocoupling to give **4d**, yielding **4c** and **4d** in a 2:3 ratio. The anti position of the allyl group in **4a**,**b** and **4d** with respect to the Cr(CO)$_3$ moiety suggests that the decomposition is not a reductive cis-elimination. During the process of purification of **4a**-**d**, it was noticed that basic activated alumina promoted irreversible quantitative isomerization of **4a**-**d** into the thermodynamically favored isomers **5a**-**d** (Scheme 1).

In conclusion, the new complexes **3a**-**c** reported here are rare examples of persistent coordinatively unsaturated Pd(II) complexes, the cohesion of which stems from a compensation of insufficient donor/acceptor Cr-Pd bonding by non-covalent interactions of preponderant attractive Coulombic nature. Even though this bonding situation is not sufficient to ensure permanent anchorage of the Pd center to the Cr(CO)$_3$ moiety, the syn-facial η^1 coordination of the indenyl ligand to Pd is thermodynamically preferred over the syn-facial and antara-facial η^3 modes. The observed fluxionality is a direct consequence of the evanescence of the polar intermetallic interaction.[9,11] These results lay the ground for further investigations of what could be considered a new concept of hemilability based on the cohesive role of non-covalent interactions (electron correlation, London force, and Coulombic attraction) in loose but manageable donor/acceptor metal-based Lewis pairs.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Computational details, experimental procedures, analytical data, and CIF files for **2**, **3a**-**c**, **4a**,**d**, and **5a**-**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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