

SUPPORTING INFORMATION

Carbonylmetallates as versatile 2-, 4- or 6-Electron Donor Metalloligands in Transition-Metal Complexes and Clusters: A Global Approach

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Computational details

Density functional theory (DFT) calculations were carried out by using the Amsterdam Density Functional (ADF2020) program suite,^[1,2] using the BP86 functional^[3-5] and a Slater-type orbital basis sets of triple-zeta plus two polarization functions quality (STO-TZ2P).^[6] The numerical integration procedure applied for the calculations was developed by te Velde et al.^[7] The frozen-core approximation was used to treat the core shells up to 1s for C, N and O, 2p for P and Cl, 3p for Co and 4p for Mo and Pd. For the heavier Mo and Pd elements, the scalar relativistic zero-order regular approximation (ZORA) was used with the associated optimized valence basis set.^[8-10] Full geometry optimizations were carried out using the analytical gradient method implemented by Versluis and Ziegler.^[11] Vibrational frequency calculations^[12,13] were performed on all the studied compounds to ascertain that the optimized structures correspond to energy minima. The bonding between the X⁻ and M_xL_n⁺ fragments in the investigated [M_xXL_n] complexes was analyzed using the Morokuma-Ziegler energy decomposition analysis (EDA) approach.^[14-17] This analysis allows to explore the nature of the interaction between the fragments through the decomposition of the total bonding energy in three components: $TBE = E_{\text{Pauli}} + E_{\text{Elec}} + E_{\text{Orb}}$, which describe the Pauli repulsion, the electrostatic interaction and the orbital interaction, respectively.^[18] Molecular orbitals and molecular structures were represented using the ADF-GUI^[2] and Molekel programs,^[19] respectively.

Table S1. Relevant computed data for the $[\text{AuX}_2]^-$ ($X = \text{Cl}, \text{Co}(\text{CO})_4, \text{MoCp}(\text{CO})_3$) series. All energies are in eV.

	$[\text{AuCl}_2]^-$		$[\text{Au}\{\text{Co}(\text{CO})_4\}_2]^-$		$[\text{Au}\{\text{MoCp}(\text{CO})_3\}_2]^-$	
Symmetry	$C_{\infty v}$		C_2		C_i	
HOMO-LUMO gap	3.45		2.87		2.98	
Fragments	$\text{AuCl} + \text{Cl}^-$		$\text{Au}[\text{Co}(\text{CO})_4] + [\text{Co}(\text{CO})_4]^-$		$\text{Au}[\text{MoCp}(\text{CO})_3] + [\text{MoCp}(\text{CO})_3]^-$	
E_{Pauli}	4.65		6.19		6.63	
E_{Elec}	-5.48		-5.61		-6.87	
E_{Orb} symmetry components	σ	-2.39	Fragmentation treated in C_1 symmetry		Fragmentation treated in C_1 symmetry	
	π	-0.46				
E_{Orb}	-2.53		-3.10		-3.09	
TBE	-3.36		-2.52		-2.33	
X⁻ frontier orbital occupations	$3p_\sigma$	1.62	σ	1.63	σ	1.49
	$3p_\pi$	2 x 1.93	π_\perp	1.94	π_\perp	1.99
			$\pi_{//}$	1.99	$\pi_{//}$	1.98

Table S2. Relevant computed data for the *trans*- $[\text{Pd}(\text{CNMe})_2\text{X}_2]$ ($X = \text{Cl}, \text{Co}(\text{CO})_4, \text{MoCp}(\text{CO})_3$) series. All energies are in eV.

	$\text{PdCl}_2(\text{CNMe})_2$		$\text{Pd}(\text{CNMe})_2\{\text{Co}(\text{CO})_4\}_2$		$\text{Pd}(\text{CNMe})_2\{\text{MoCp}(\text{CO})_3\}_2$	
Symmetry	C_{2v}		C_s		C_{2h}	
HOMO-LUMO gap	2.26		1.71		1.83	
Fragments	$[\text{PdCl}(\text{CNMe})_2]^+ + \text{Cl}^-$		$[\text{Pd}(\text{CNMe})_2\{\text{Co}(\text{CO})_4\}]^+ + [\text{Co}(\text{CO})_4]^-$		$[\text{Pd}(\text{CNMe})_2\{\text{MoCp}(\text{CO})_3\}]^+ + [\text{MoCp}(\text{CO})_3]^-$	
E_{Pauli}	3.89		3.65		4.71	
E_{Elec}	-7.32		-5.73		-6.29	
E_{Orb} symmetry components	a_1	-2.41	Fragmentation treated in C_1 symmetry		Fragmentation treated in C_s symmetry	
	a_2	-0.05				
	b_1	-0.24			a'	-2.80
	b_2	-0.24		a''	-0.41	
E_{Orb}	-2.94		-2.86		-3.21	
TBE	-6.37		-4.94		-4.79	
X⁻ frontier orbital occupations	$3p_\sigma (a_1)$	1.50	σ	1.33	$\sigma (a')$	1.32
	$3p_{\pi_\perp} (b_1)$	1.94	π_\perp	1.95	$\pi_\perp (a')$	1.98
	$3p_{\pi_{//}} (b_2)$	1.96	$\pi_{//}$	1.99	$\pi_{//} (a'')$	1.97

Table S3. Relevant computed data for the $\text{Pd}_2(\text{PH}_3)_2(\mu\text{-X})_2$ ($\text{X} = \text{Cl}, \text{Co}(\text{CO})_4, \text{MoCp}(\text{CO})_3$) series. All energies are in eV.

	$\text{Pd}_2(\text{PH}_3)_2\text{Cl}_2$		$\text{Pd}_2(\text{PH}_3)_2[\text{Co}(\text{CO})_4]_2$		$\text{Pd}_2(\text{PH}_3)_2[\text{MoCp}(\text{CO})_3]_2$	
Symmetry	C_i		C_i		C_i	
HOMO-LUMO gap	2.56		2.40		2.55	
Fragments	$[\text{Pd}_2(\text{PH}_3)_2\text{Cl}]^+ + \text{Cl}^-$		$[\text{Pd}_2(\text{PH}_3)_2\{\text{Co}(\text{CO})_4\}]^+ + [\text{Co}(\text{CO})_4]^-$		$[\text{Pd}_2(\text{PH}_3)_2\{\text{MoCp}(\text{CO})_3\}]^+ + [\text{MoCp}(\text{CO})_3]^-$	
E_{Pauli}	8.04		17.18		12.17	
E_{Elec}	-11.12		-12.17		-12.51	
E_{Orb}	-3.90		-5.39		-5.91	
TBE	-6.98		-6.38		-6.25	
X frontier orbital occupations	σ	1.64	σ	1.40	σ	1.48
	π_{\perp}	1.69	π_{\perp}	1.72	π_{\perp}	1.68
	$\pi_{//}$	1.91	$\pi_{//}$	1.95	$\pi_{//}$	1.92

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