

A Theoretical Search for Stable Terminal Carbides

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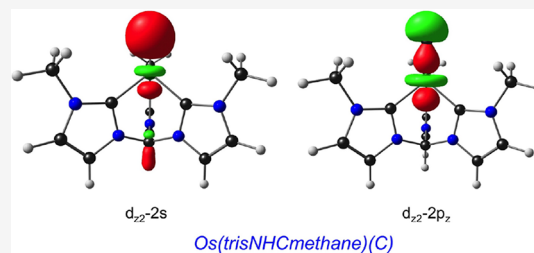
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ABSTRACT: Exploratory scalar-relativistic density functional theory (B3LYP*-D3/ZORA-STO-TZ2P) calculations have been used to examine the stability and bonding of pseudotetrahedral Group 8 (Fe, Ru, and Os) and Group 9 (Co, Rh, and Ir) terminal carbide complexes with d_8^4 ground states and tripodal tris(*N*-heterocyclic-carbene) supporting ligands. The calculations predict relatively low adiabatic ionization potentials of 4.3–5.9 eV for the charge-neutral species and sizable adiabatic singlet–triplet gaps in the 0.9–1.6 eV range. Furthermore, the complexes exhibit near-zero or negative electron affinities, indicating at least moderate reductive stability. The calculated results suggest that, once successfully synthesized, the majority of the complexes examined should be isolable and moderately stable. As far as the bonding in the metal–carbido moiety is concerned, natural bond orbital (NBO) analyses suggest a triple bond, with a 2s-like lone pair on the carbido carbon.



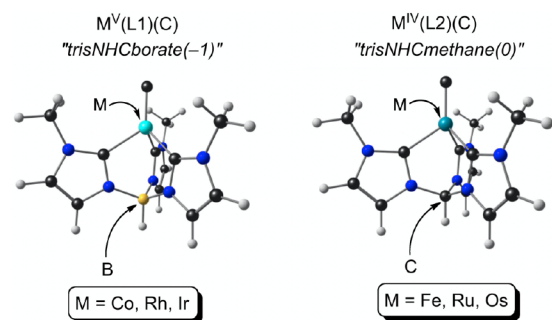
INTRODUCTION

Terminal transition metal carbides are exceedingly rare.^{1,2} The handful of examples known to date hail from Groups 6 and 8, including $[\{N(R)Ar\}_3Mo(\equiv C:)]^-$, $[Tp^*(CO)_2M(\equiv CLi)]$ ($M = W, Mo$; $Tp^* = 3,5$ -dimethyltris(pyrazolyl)borate),^{3–6} $[M(\equiv C:)(L)_2(X)_2]$ ($M = Ru$ and Os),^{7–10} and $[P_2Mo(\equiv C:)(CO)]^{+,0,-}$ ($P_2 =$ a terphenyl-diphosphine ligand).^{11,12} For square-pyramidal and octahedral complexes, a “carbido wall” (analogous to the oxo wall) appears to apply at a d-electron count of 2, corresponding to a d_8^2 electronic configuration. Thus, Group 8 (Fe, Ru, and Os) $M(VI)$ -carbido porphyrins¹³ and an Ir(VII)-carbido corrole¹⁴ have been postulated as potentially synthesizable. Higher d-electron counts of up to 4 are conceivable for pseudotetrahedral complexes, corresponding to a d_8^4 electronic configuration.^{15,16} Little, however, is known about the actual stability of such complexes or their excited-state energetics. To shed light on the question, we examined a series of d^4 pseudotetrahedral tris(*N*-heterocyclic-carbene) transition metal carbides and nitrides with density functional theory (DFT) calculations. The nitrido complexes examined are simplified analogs of stable, experimentally well-characterized systems^{17–20} and have been included here as calibration for our calculations on the speculative carbido systems. Based on their singlet–triplet gaps and electron affinities (EAs), several of the terminal carbides examined are indeed expected to be thermodynamically stable and hence worthwhile synthetic targets.^{21,22}

RESULTS AND DISCUSSION

Two different tripodal tris(carbene) ligands were investigated: an anionic ligand L1 with a BH anchor (tris-NHCborate) and a neutral ligand L2 with a CH anchor (tris-NHCmethane). Scheme 1 depicts the molecules studied, and Table 1 presents

Scheme 1. Terminal Carbides Studied in This Work



key DFT (B3LYP*-D3/ZORA-STO-TZ2P) results. The results encompass five four experimentally observable quantities, namely, bond distances and angles, adiabatic ionization potentials (IPs), EAs, and singlet–triplet gaps. None of the species examined evinced unduly small HOMO–LUMO gaps (or singlet–triplet gaps) so no pressing need was apparent for the deployment of multiconfigurational methods.

As expected for terminal carbides, our calculations predict short axial $M-C_{\text{carbido}}$ bonds, which hover around 1.5 Å for Fe and Co, around 1.64 Å for Ru and Rh, and around 1.68 Å for Os and Ir. These distances are only slightly longer (by 0.01–0.02 Å) than the axial $M-N_{\text{nitrido}}$ complexes calculated for the

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Table 1. Selected B3LYP*-D3/ZORA-STO-TZ2P Results for the Molecules Studied^a

	$d(M-L_{ax})$ (Å)	$d(M-C_{carbene})$ (Å)	$\theta(L_{ax}-M-C_{carbene})$ (deg)	IP (eV)	EA (eV)	E_{S-T} (eV)	BO
Co(L1)(C)	1.516	1.920	121.5	5.623	-0.185	0.892	2.686
Rh(L1)(C)	1.627	2.104	126.0	5.849	-0.393	1.444	2.751
Ir(L1)(C)	1.672	2.067	124.9	5.698	-0.031	1.210	2.755
Fe(L1)(N)	1.498	1.915	122.2	5.406	0.013	0.479	2.738
Ru(L1)(N)	1.619	2.064	126.3	5.666	-0.177	1.161	2.729
Os(L1)(N)	1.655	2.038	125.0	5.566	0.133	1.020	2.696
Fe(L2)(C)	1.527	1.876	122.0	4.343	-0.976	1.305	2.835
Os(L2)(C)	1.691	2.015	124.8	4.843	-0.818	1.459	2.822
Ru(L2)(C)	1.649	2.047	126.0	4.706	-0.888	1.650	2.871

^a $L_{ax} = C$ or N ; $C_{carbene}$ refers to the carbene center in the tris(carbene) ligand; and BO refers to the Mayer bond order.

$M(L1)(N)$ series (for $M = Fe$, the optimized $Fe-N$ distance of 1.498 Å is in near-perfect agreement with a crystallographic value of 1.499(5) Å observed for a closely related compound, $PhB(MesIm)_3Fe \equiv N^{19}$). In an interesting reversal, the $M-C$ single bonds involving ligands L1 and L2 are slightly longer for Ru and Rh than their 5d congeners, Os and Ir, respectively. We have not examined the origin of this reversal, but Pyykkö's covalent radii^{23–25} echo a similar effect. Thus, while the double- and triple-bond covalent radii of Ir (1.15 and 1.07, respectively) are longer than those of Rh (1.10 and 1.06, respectively), the single bond covalent radius of Ir (1.22) is shorter than that of Rh (1.25 Å).

The complexes in the $M(L1)(C)$ and $M(L1)(N)$ series ($M = Co, Rh, \text{ and } Ir$) exhibit “healthy” (i.e., not unduly low) IPs in the 5–6 eV range that are consistent with their existence as stable compounds. The $M(L2)(C)$ series ($M = Fe, Ru, \text{ and } Os$) does exhibit lower IPs in the 4–5 eV range, indicating a certain sensitivity to oxidation. By way of perspective, many electron-rich but air-stable porphyrin-type molecules such as tetrabenzoporphyrin exhibit IPs in the 5–6 eV range.^{26–29}

Interestingly, none of the compounds examined exhibit a significant adiabatic EA. In fact, the majority of them exhibit negative EAs, and the molecules in the $M(L2)(C)$ series exhibit exceptionally large, negative EAs for neutral molecules. In other words, these complexes are not expected to give rise to stable gas-phase anions and in solution are expected to exhibit unusually low reduction potentials. The compounds thus, are all predicted to be stable under moderately reductive conditions.

In light of the frontier orbital theory,^{30,31} HOMO–LUMO gaps and singlet–triplet gaps provide a popular and well-justified measure of a molecule's reactivity. The low calculated singlet–triplet gap of around 0.5 eV for $Fe(L1)(N)$ is consistent with the relatively reactive nature of analogous compounds with stabilized carbene-type species such as CO and isocyanides. Notably, an S–T gap of almost 0.9 eV is predicted for $Co(L1)(C)$, while even higher S–T gaps >1 eV are predicted for the other carbido complexes examined, strongly suggesting that these complexes should exist as stable compounds.

Finally, we examined the affinity of the complexes for the Lewis acid BF_3 . In terms of electronic energy, the affinities proved small, on the order of a couple of tenths of an eV. However, it proved surprisingly difficult to confirm the adducts as minima, in that they were found to exhibit multiple imaginary frequencies. We were thus led to conclude that the terminal carbides studied are not particularly Lewis-basic, indicating that they should be isolable and stable under relatively ordinary conditions.

As for the question of metal–carbon quadruple bonding^{32,33} in the terminal carbides examined, four canonical MOs indeed

exhibit a significant $M-C_{carbido}$ bonding: the two $M(d_{\pi})-C(p_{\pi})$ π -bonding MOs, a predominantly $d_{z^2}-p_z$ -based σ -bonding MO, and a predominantly $d_{z^2}-2s$ -based σ -bonding MO (Figure 1).

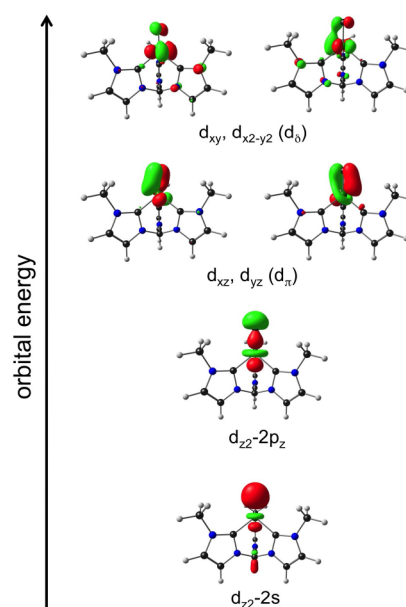


Figure 1. Selected occupied Kohn–Sham MOs for the Al–H bond for $Os(L2)(C)$.

The NBO analysis, however, indicates only three MOs with a predominant $M-C_{carbido}$ bonding character, namely, two π and one σ NBO, along with a 2s-like lone pair on the carbide carbon. This result stands in sharp contrast to the scenario found for diatomics such as RhB ,^{34–37} for which the NBO analysis clearly indicates a quadruple bond (including two σ NBOs). Evidently, the second σ NBO does not survive in the presence of the strongly σ -donating tris(carbene) supporting ligands employed in this study. Given our preoccupation with the question of stability and isolability (as opposed to bonding), an additional analysis of the bonding was not undertaken at this point. We hope to return to the question following the successful synthesis of some of the complexes studied.

CONCLUSIONS

In conclusion, DFT calculations predict stable, pseudotetrahedral, d^4 terminal carbide complexes with tripodal tris(N -heterocyclic-carbene) supporting ligands. All of the complexes examined exhibit sizable singlet–triplet gaps and very small or negative EAs. They also do not appear to exhibit a significant affinity for the Lewis acid BF_3 . A few of the complexes are

predicted to exhibit low IPs in the order of 4.5 eV, indicating that they should be susceptible to oxidation. Finally, unlike in diatomics such as RhB, NBO analyses afforded no indication of a quadruple bond for the metal carbide moiety in any of the complexes studied.

COMPUTATIONAL METHODS

All structures were optimized in gas phase with the scalar-relativistic ZORA³⁸ Hamiltonian, the B3LYP^{39,40} exchange-correlation functional, Grimme's D3⁴¹ dispersion corrections, and all-electron ZORA Slater-type TZ2P basis sets, all as implemented in the ADF program system.⁴² The tightest practicable criteria were used for both SCF and geometry cycles, as well as for frequency analyses; the latter established the optimized structures as true minima. All energies, including IPs, EAs, and E_{S-T} 's, are adiabatic values, obtained via a Δ SCF method, i.e., as differences in total electronic energy between the two states of interest. In general, the neutral complexes were all found to conform to C_{3v} symmetry, but the ionized and triplet states conformed only to C_s , as a result of Jahn–Teller distortions. Several of the systems were also examined with OLYP^{43,44}-D3 calculations, and agreement with B3LYP*-D3 was generally found to be excellent (as also observed elsewhere.^{45,46} None of the species examined evinced unduly small HOMO–LUMO gaps (or singlet–triplet gaps), hence no compelling need was apparent for the deployment of multiconfigurational methods. NBO analyses were performed based on the single-point OLYP-D3 calculations on the B3LYP*-D3 optimized geometries.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.3c00363>.

Optimized DFT coordinates (XYZ)

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Notes

The authors declare no competing financial interest.

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