

Theoretical Investigation of Triple Bonding between Transition Metal and Main Group Elements in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{ER}$ (M = Cr, Mo, W; E = Si, Ge, Sn, Pb; R = Terphenyl Groups)

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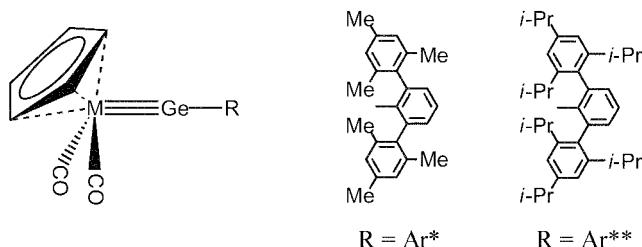
To extend the knowledge of triple bonding between group 6 transition metal and heavier group 14 elements, the structural and bonding aspects of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{ER}$ (M = Cr, Mo, W; E = Si, Ge, Sn, Pb) are investigated by hybrid density functional calculations at the B3PW91 level. Substituent effects are also investigated with R = H, Me, SiH₃, Ph, C₆H₃-2,6-Ph₂, C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂, and C₆H₃-2,6-(C₆H₂-2,4,6-*i*Pr₃)₂.

Key Words : Triple bonds, Group 6 transition metals, Group 14 elements, Density functional calculations

Introduction

Since the first synthesis of a stable disilene (R₂Si=SiR₂) in 1981,¹ a variety of stable heavier analogues of alkenes, R₂E=ER₂ (E = Si, Ge, Sn, even Pb), have been synthesized and isolated up to now.² In contrast, the stable heavier analogues of alkynes (RE≡ER) possessing a distinct triple bond are still quite rare, despite several theoretical calculations³ and experimental attempts.⁴ It has been known that RE≡ER does not take a linear-structure but prefers a highly trans-bent structure in which the E-E distance is significantly elongated, as E becomes heavier.^{3,5,6} Thus, stable compounds containing a distinct triple bond to heavier group 14 elements have attracted special interest as synthetic targets in main group chemistry.⁷

Power and co-workers have recently reported the synthesis and isolation of a series of novel group 6 transition metal germylene complexes, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{GeR}$ (M = Cr, Mo, W; R = 2,6-bis(2,4,6-trimethylphenyl)phenyl (Ar*), 2,6-bis(2,4,6-triisopropylphenyl)phenyl (Ar**)).⁸



The *m*-terphenyl groups Ar* and Ar** have been known as representative bulky groups useful for the synthesis and stabilization of multiply bonded species.⁹ According to X-

ray crystallographic analysis, the central M-Ge distances are 2.167 Å for M = Cr, 2.271-2.272 Å for M = Mo, and 2.277 Å for M = W. These bond distances are very short and deserve to be a triple bond, compared with the M-Ge single bond distances of 2.590 Å for M = Cr and 2.681 Å for M = W observed for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M-GeAr}^{**}$.^{8b} It is noticeable that the M-Ge-R linkage is almost linear (170.9°-176.0°).^{8b}

To extend the knowledge of transition metal-main group triple bonding, we have investigated all combinations of group 6 metals (M = Cr, Mo, W) and heavier group 14 elements (E = Si, Ge, Sn, Pb) for the $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{ER}$ system using density functional calculations. Effects of substituents (R) on the M-E bonding are also investigated. It is suggested that even triple bonds to the heaviest Pb atom are interesting synthetic targets.

Computational Details

Geometries are fully optimized with hybrid density functional theory at the B3PW91 level using the Gaussian 98 program package.¹⁰ In the B3PW91 calculation, Becke's 3-parameter nonlocal exchange functional (B3)¹¹ was used together with the exact (Hartree-Fock) exchange functional in conjunction with the nonlocal correlation functional of Perdew and Wang (PW91).¹² Effective core potentials (ECPs) and LANL2DZ basis sets developed by Hay and Wadt¹³ were employed for Cr, Mo, and W. The LANL2DZ basis sets for Si, Ge, Sn, and Pb were augmented by two sets of d polarization functions (d exponents 0.424 and 0.118 for Si, 0.382 and 0.108 for Ge, 0.253 and 0.078 for Sn, and 0.213 and 0.062 for Pb).¹⁴ The split-valence d-polarized 6-31G(d) basis sets were employed for C, O, and H.¹⁵

Results and Discussion

Since the structure of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$ has been determined by X-ray crystal analysis,^{8b} its geometry optimization was first carried out to calibrate the B3PW91

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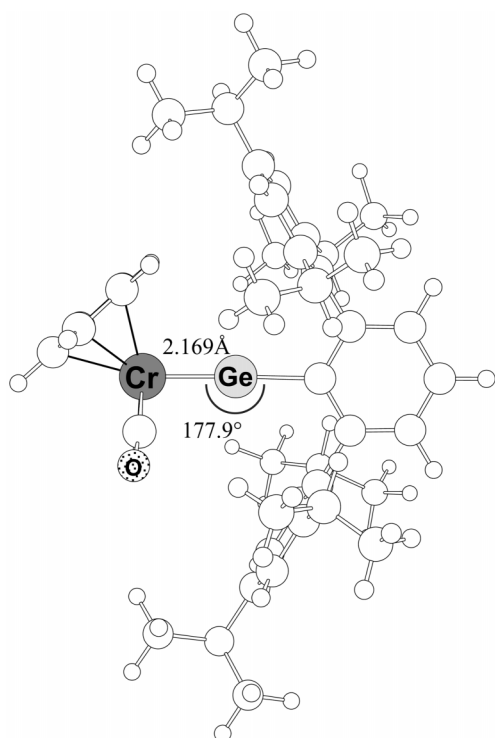


Figure 1. The optimized structure of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$.

calculations. As shown in Figure 1, the calculated Cr-Ge distance and the Cr-Ge-Ar** angle are 2.169 Å and 177.9°, respectively. These values are very close to those of 2.167 Å and 176.0° observed for the X-ray crystal structure.^{8b} The calculated Cr-C (C in η^5 -cyclopentadienyl) average distance of 2.192 Å and C=O distance of 1.165 Å also agree very well with the X-ray values of 2.190 Å and 1.151 Å, respectively. These results suggest that B3PW91 calculations are reliable enough for the present purpose.

The orbital analysis of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$ reveals that three important orbitals are formed between Cr and Ge, as clearly shown in Figure 2. One of them is a σ type bonding orbital that consists mainly of d (Cr) and p (Ge) atomic orbitals. The other two are in-plane and out-of plane π type bonding orbitals consisting of d (Cr) and p (Ge) atomic orbitals, which are denoted as π_{in} and π_{out} , respectively. Obviously, these three orbitals contribute to the formation of a triple bond between Cr and Ge. Accordingly, the energy required to cleave the Cr-Ge bond (leading to two $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}$ and GeAr^{**} fragments in the $^2\text{A}''$ and $^2\Pi$ ground states, respectively) was calculated to be as large as 55.1 kcal/mol. This value is much larger than the corresponding energy of 27.9 kcal/mol calculated for the Cr-Ge single bond in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Cr-GeAr}^{**}$, owing to the three bonding orbitals (σ , π_{in} , and, π_{out}) between Cr and Ge in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$.

The three Cr-Ge bonding orbitals in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$ originate from the orbital interactions between the component parts, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}$ and GeAr^{**} in the $^2\text{A}''$ and $^2\Pi$ ground states. As is apparent from the orbital interactions in Figure 3, the largest overlapping of orbitals is

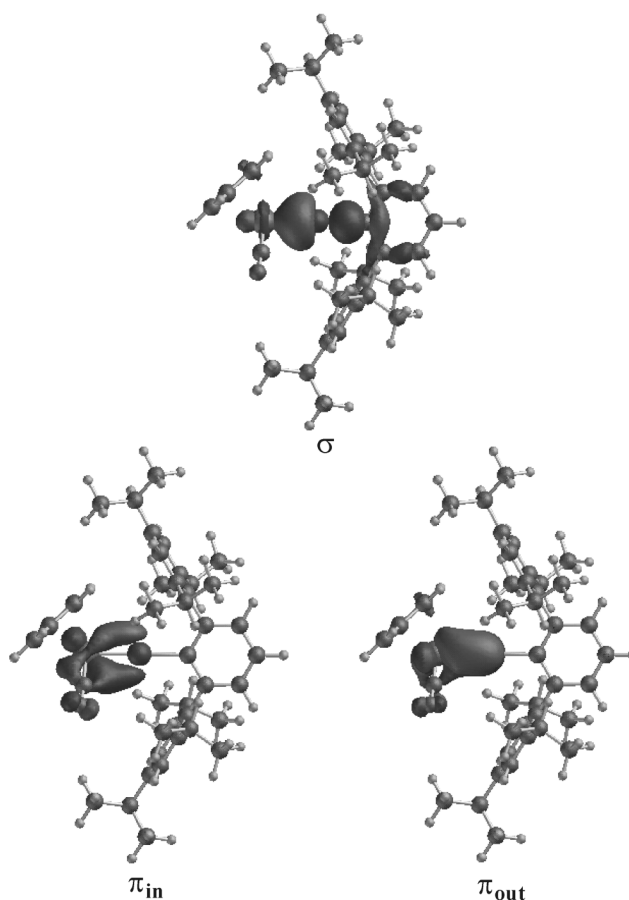


Figure 2. Three important bonding orbitals between Cr and Ge in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$.

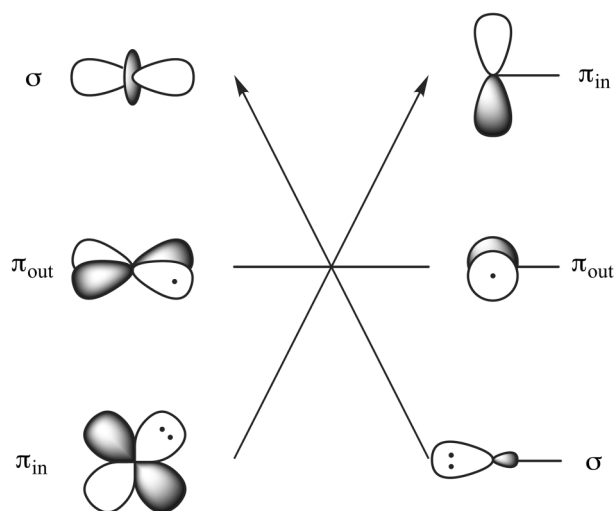


Figure 3. Orbital interactions between $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}$ and ER components in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{ER}$.

obtained between Cr and Ge, when the Cr-Ge-Ar** linkage becomes linear. This is a reason why an almost linear Cr-Ge-Ar** linkage is favored in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeAr}^{**}$. This bonding situation differs significantly from the situation for $\text{RE}\equiv\text{ER}$ in which a highly trans-bent structure with an elongated E-E distance is favored, as is obvious from the

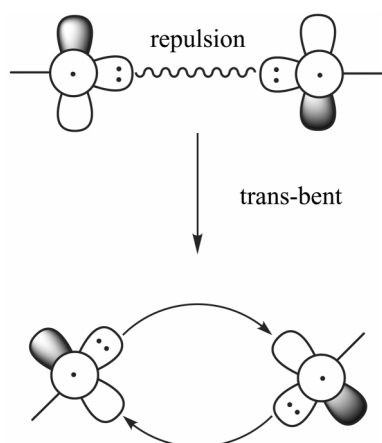


Figure 4. Orbital interactions between two ER components in RE=ER.

orbital interactions in Figure 4.

To investigate the effects of substituents, geometry optimization was carried out for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeR}$ with R = H, Me, SiH₃, Ph, Ar*, and Ar**, all these groups are electronegative for Ge, except for SiH₃ that is somewhat electropositive. To see the effect of Me and *i*Pr on the Ar* and Ar** groups, the *m*-terphenyl group lacking Me and *i*Pr was also considered, which is denoted hereafter as Ar (=C₆H₃-2,6-Ph₂). The optimized key geometrical parameters, Mulliken charges on Cr and Ge, and binding energies are summarized in Table 1. It is noteworthy that all the Cr-Ge distances are in the range of 2.160–2.169 Å, regardless of R, except for the shorter distance of 2.157 Å for R = H. However, the Cr-Gr-R angles depend on R. As R becomes bulkier, the Cr-Gr-R linkage becomes gradually linear; 158.0° for R = H, 159.0° for R = Me, and 166.0° for R = Ph. It is interesting that bulkier terphenyl groups make the Cr-Ge-R angles almost equal to 180°; 174.4° for R = Ar, 174.8° for R = Ar*, and 177.9° for R = Ar**.

Against the orbital interactions in Figure 3, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeR}$ takes a significantly bent Cr-Ge-R linkage, when R is small. This is because the orbitals on Ge can interact with the π^* orbitals on C=O ligands as well as the d

Table 1. Key geometrical parameters^a and Mulliken charges on Cr and Ge, and binding energies (BE^b) calculated for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeR}$ (R = H, Me, SiH₃, Ph, Ar, Ar*, and Ar**)

R	symmetry	Cr-Ge	Cr-Ge-R	charge		BE
				Cr	Ge	
H	C ₁	2.157	158.0	-0.315	0.252	58.5
Me	C _s	2.161	159.0	-0.348	0.453	60.8
SiH ₃	C ₁	2.165	155.7	-0.392	-0.001	59.2
Ph	C _s	2.160	166.0	-0.387	0.423	57.6
Ar ^c	C ₁	2.169	174.4	-0.449	0.427	52.6
Ar* ^d	C ₁	2.164	174.8	-0.449	0.430	55.5
Ar** ^e	C ₁	2.169	177.9	-0.445	0.424	55.1

^aDistances in Å and angles in degrees. ^bBinding energies in kcal/mol. ^cAr = C₆H₃-2,6-Ph₂. ^dAr* = C₆H₃-2,6-(C₆H₂-2,4,6-Me₃)₂. ^eAr** = C₆H₃-2,6-(C₆H₂-2,4,6-*i*Pr₃)₂.

Table 2. Key geometrical parameters^a and binding energies (BE^b) calculated for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{EH}$ (M = Cr, Mo, and W; E = Si, Ge, Sn, and Pb)

	E			
	Si	Ge	Sn	Pb
M = Cr				
Cr-E	2.080	2.157	2.336	2.369
Cr-E-H	151.0	158.0	155.6	160.3
BE	68.1	58.5	46.7	41.5
M = Mo				
Mo-E	2.213	2.292	2.467	2.500
Mo-E-H	163.6	165.2	162.7	165.0
BE	85.9	76.3	64.8	58.8
M = W				
W-E	2.222	2.297	2.470	2.498
W-E-H	173.3	173.3	171.0	172.2
BE	99.9	89.3	75.9	69.0

^aDistances in Å and angles in degrees. ^bBinding energies in kcal/mol.

orbitals on Cr, as is apparent from the π_{in} orbital density map in Figure 2. However, the weak attraction between Ge and C=O is easily overcome by steric repulsion between R and C=O, as R becomes bulkier. This is a reason why bulky substituents such as Ar* and Ar** are important to realize a linear Cr-Ge-R linkage. In addition, it is instructive to note that bulky substituents help to protect the central Cr-Ge triple bond from reactive reagents.

It is general that binding energies become smaller as substituents become bulkier, because of steric repulsions. However, the Cr-Ge binding energies calculated for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Cr}\equiv\text{GeR}$ do not depend significantly on R, as indicated by the values of 58.5 kcal/mol for R = H, 60.8 kcal/mol for R = Me, 57.6 kcal/mol for R = Ph, 52.6 kcal/mol for R = Ar, 55.5 kcal/mol for R = Ar*, and 55.1 kcal/mol for R = Ar**. Even the binding energy for R = Ar** differs only by 3.4 kcal/mol from that for R = H. This may be ascribed to the fact that bulky substituents help to make the Cr-Ge-R linkage linear.

We next investigated whether the M-E binding energies in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{ER}$ are significantly changed, when M and E are changed in the way Cr → Mo → W and Si → Ge → Sn → Pb. For this purpose, the R = H case was considered, because the binding energies do not depend strongly on the kind of R, as already described. The key geometrical parameters and M-E binding energies calculated for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{EH}$ are summarized in Table 2. The M-E binding energies become considerably small, as E becomes heavier. As is apparent from Figure 5, it is because the energy difference between the singly occupied π_{out} orbitals on M and ER parts is increased and the electron-accepting π_{in} orbital on ER lies higher in energy, as E becomes heavier; it appears that the stabilization due to the energy closeness of s orbitals on M and ER is small because of a large energy gap. In contrast, the M-E binding energies are greatly enlarged, as M becomes heavier. This is because the π_{in} and π_{out} orbitals on M lie higher in energy and interact more

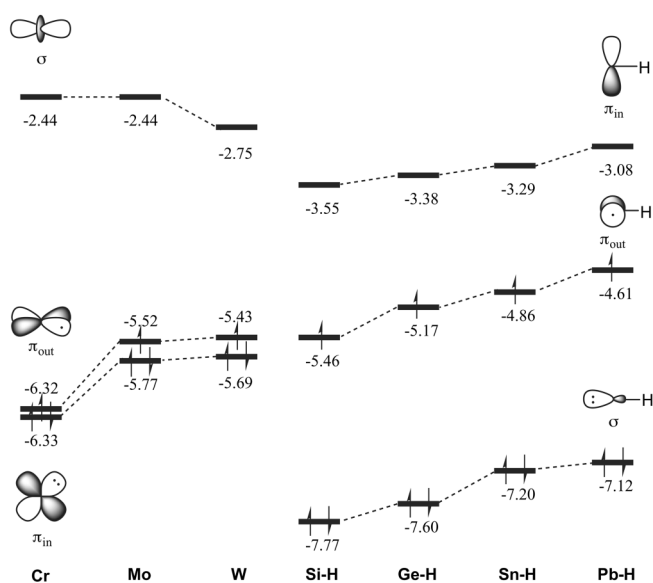


Figure 5. Orbital levels (eV) of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}$ and EH fragments in the ground states.

Table 3. Key geometrical parameters^a and binding energies (BE^b) calculated for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{PbAr}^{**}$ (M = Cr, Mo, and W)

	M		
	Cr	Mo	W
M-Pb	2.383	2.513	2.516
M-Pb-Ar ^{**}	176.8	178.2	179.2
BE	41.1	57.2	67.3

^aDistances in Å and angles in degrees. ^bBinding energies in kcal/mol.

strongly with the π_{in} and π_{out} orbitals on ER, as M becomes heavier. Therefore, the strongest triple bond is formed when M = W and E = Si, its binding energy being as large as 99.9 kcal/mol.

We now focus on triple bonds to the Pb atom that is the heaviest in group 14. Triple bonds to Pb are still unknown in a stable form, despite several synthetic attempts. For example, the shortest Pb-Pb distance observed up to now for the lead analogues of alkenes, R_2PbPbR_2 , is 2.903 Å, which differs little from the Pb-Pb single bond distances of ca. 2.9 Å.¹⁶ There is only one synthetic example for the lead analogues of alkynes, RPbPbR .⁶ However, the observed Pb-Pb distance is as long as 3.188 Å. Therefore, triple bonds to Pb are currently of considerable interest in main group chemistry. The key geometrical parameters and binding energies calculated for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{PbAr}^{**}$ (M = Cr, Mo, W) are presented in Table 3. It is noteworthy that the M-Pb distances of 2.383 Å for M = Cr, 2.513 Å for M = Mo, and 2.516 Å for M = W are much shorter than the corresponding single bond distances of 2.909 Å for M = Cr, 2.985 Å for M = Mo, and 2.981 Å for M = W observed for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M-PbAr}^{**}$.¹⁷ In addition, the M-Pb-Ar^{**} angles of 176.8–179.2° for $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{PbAr}^{**}$ are very close to 180°. These results suggest that Pb is able to form a strong triple bond in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{PbAr}^{**}$. It should be noted that the M-Pb binding energies of 41–67 kcal/mol

are much larger than the Pb-Pb binding energy of 22 kcal/mol calculated¹⁸ for the synthesized $\text{Ar}^*\text{PbPbAr}^*$ compound.⁶

Power and co-workers have synthesized, for example, $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{GeAr}^{**}$, by eliminating the CO ligand from $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{M-GeAr}^{**}$. The CO elimination occurs easily under mild conditions. However, it does not take place for E = Sn and Pb. Accordingly, for example, it was calculated for M = Cr that the CO elimination energies becomes large as E becomes heavier; 23.9 kcal/mol for E = Si, 28.5 kcal/mol for E = Ge, 37.2 kcal/mol for E = Sn, and 39.9 kcal/mol for E = Pb. Although Power and co-workers have attempted to induce C=O elimination by introducing bulky groups on cyclopentadienyl, it has been unsuccessful.¹⁹ In this context, another synthetic route *via* N_2 elimination²⁰ may be interesting for the synthesis of $\text{M}\equiv\text{Pb}$ triple bonds, because a $\text{W}\equiv\text{Sn}$ triple bond is very recently synthesized successfully by the synthetic route.²¹

Conclusion

Density functional calculations at the B3PW91 level reveal the interesting structural and bonding aspects of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{ER}$ (M = Cr, Mo, W; E = Si, Ge, Sn, Pb). The M-E triple bond consisting of one σ and two π orbitals becomes the strongest when M = W and E = Si.²² Bulky *m*-terphenyl groups make an important contribution to the linearization of the M-E-R linkage.²³ Unlike the lead analogues of alkynes, distinct triple bonds to Pb are realized in $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{PbR}$. It is expected that new various synthetic methods will be soon developed and open up an interesting area in the chemistry of transition metal-main group triple bonding.

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