Table I. Atom Coordinates (Space Group *Fdd*2)

	x	*y*	*z*
Rh	0.0379	0.1374	0.8777
Fe	0.0661	0.0678	1.0192
P(1,3)	0.0744	0.1559	0.9058
P(2,4)	0.0589	−0.0277	1.0777
O(1,4)	0.0451	0.0168	0.7384
O(2,5)	0.1126	0.0563	1.0954
O(3,6)	0.0444	0.1205	1.2846
C(1)	0.0519	0.0460	0.8369
C(2)	0.0939	0.0605	1.0606
C(3)	0.0520	0.1000	1.1765
C(4)	0.0790	−0.0845	1.0047
C(5,7)	0.0992	−0.0940	1.1142
C(6)	0.0890	−0.0630	0.8480
C(7,5)	0.0666	−0.1440	0.9719
C(8)	0.0504	−0.0455	1.2788
C(9,10)	0.0672	−0.0185	1.3942
C(10,9)	0.0475	−0.1140	1.3165
C(11)	0.0268	−0.0185	1.3052
C(12)	0.0814	−0.2210	1.0368
C(13,15)	0.0585	0.2430	1.1115
C(14)	0.0971	0.2005	1.1696
C(15,13)	0.0920	0.2735	0.9555
C(16)	0.0944	0.1570	0.7361
C(17,19)	0.0900	0.0995	0.6386
C(18)	0.0908	0.2095	0.6252
C(19,17)	0.1190	0.1550	0.7895
C(20)	0.0262	0.2145	0.7572
C(21)	0.0272	0.1665	0.6540
C(22)	0.0068	0.1320	0.6038
C(23)	−0.0032	0.0895	0.7092
C(24)	0.0045	0.0900	0.8750
C(25)	0.0025	0.1370	0.9690
C(26)	−0.0082	0.1955	0.9318
C(27)	0.0042	0.2355	0.8358

The crystal structure of the title compound, $C_{27}H_{49}FeO_3P_2Rh$, was described[2] as monoclinic, space group *Cc*, with $a = 8.735$ (2) Å, $b = 22.720$ (3) Å, $c = 30.485$ (4) Å, $\beta = 98.28$ (2)°, and $Z = 8$. It is properly described as orthorhombic, space group *Fdd*2. The vectors (-1,0,-2), (0,1,0), and (1,0,0) describe a face-centered cell with $a' = 60.334$ Å, $b' = 22.720$ Å, $c' = 8.735$ Å, $\beta' = 90.04° \rightarrow 90°$ ($\alpha' = \gamma' = 90°$), and $Z = 16$; the corresponding coordinate transformations are $x' = -{}^1/_2 z + 0.0494$, $y' = y + {}^1/_8$, and $z' = x - {}^1/_2 z$. After applying these transformations to the coordinates in Table II of ref 2 and appropriately averaging over the two independent molecules in *Cc*, we obtain the coordinates in Table I; the average coordinate shift involved in the averaging was less than 1.0σ. The process was somewhat complicated because the coordinates in Table II, ref 2, do not correspond to discrete molecules (several atoms must be moved to other asymmetric units).

The statement[2] that "the Rh atom ... has a roughly square-planar coordination" is incorrect in its context: the constellation of cited atoms Rh, P(1,3), C(1), and the midpoints M (C(20) and C(21)) and M′ (C(23) and C(24)) of the two double bonds of the COD ligand is perhaps more nearly tetrahedral than planar (the dihedral angle between the planes P–Rh–C and M–Rh–M′ is 61°). The six "bond" angles are 80, 107, 163, 123, 99, and 88° (in the order P–Rh–C(1), P–Rh–M, P–Rh–M′, etc.), while the perpendicular displacements from the least-squares plane range from 0.30 to 0.73 Å. However, atoms Rh, Fe (instead of C(1)), P(1,3), M, and M′ *are* (slightly twisted) coplanar, with respective deviations 0.03, −0.25, 0.27, −0.23, and 0.17 Å from their least-squares plane and rough twofold symmetry (angles 107 and 112° at P(1,3)–Rh–M and Fe–Rh–M′). Atom C(1), which in any case[2] is only weakly bonded to Rh, lies −1.68 Å off the plane.

The sets of out-of-plane deviations in footnote 17, ref 2, are entirely different not only from the set found here (but not quoted) for the corresponding averaged atoms but also from each other, and this last in spite of the approximate structural identity of the two molecules already noted on p 507, column 2, of ref 2, and the actual equivalence demonstrated here. The two planes of ref 2 apparently were derived directly from the published coordinates and hence involve atoms in various molecules—and not the same selection of atoms (equivalent by symmetries of *Cc*) for the two.

No other substantial changes in the description of the structure need to be made other than to note that there is only one molecule in the asymmetric unit, so that all the molecules are structurally equivalent.

Registry No. (t-Bu_2PH)$(CO)_2Fe(\mu$-$CO)(\mu$-t-$Bu_2P)Rh(COD)$, 106681-53-2.

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[2] Arif, A. M.; Chandler, D. J.; Jones, R. A. *Organometallics* 1987, *6*, 506.

On the Existence of Methylborylene. An ab Initio Investigation of the CBH_3 Potential Energy Surface

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Summary: Methylborylene, CH_3–B:, is a minimum on the potential energy surface. Although $CH_2{=}BH$ is 24.3 kcal/mol more stable (MP4/SDTQ/6-311G**//6-31G*), the 1,2-H shift barrier is indicated to be 25.0 kcal/mol. As higher levels of theory are not expected to reduce this value appreciably, it should be possible to observe methylborylene under appropriate experimental conditions. This contrasts with the carbene analogue CH_3–CH:, which is predicted to rearrange to ethylene without any appreciable barrier. Similarly, the boron-substituted singlet carbene H_2B—CH:, although stabilized by π-delocalization ($H_2B^-{=}CH^+$), is not indicated to be a stable species when electron correlation corrections are taken into consideration. Rearrangement into $CH_2{=}BH$, the simplest compound with a C═B double bond, is predicted to occur without activation. The entire triplet CBH_3 potential energy surface is indicated to lie above the singlet surface. The singlet–triplet energy separation in BH (31.8 kcal/mol at the highest level of theory) is increased by 11.8 kcal/mol in CH_3B due to methyl substitution.

In the presence of C_8K (intercalated potassium–graphite), methylboron dibromide, CH_3BBr_2, reacts with acetylenes and with olefins to give a variety of organoboron compounds with intriguing structures.[1-3] Some of these

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[1] van der Kerk, S. M.; Boersma, G. J.; van der Kerk, G. J. M. *Tetrahedron Lett.* 1976, 4765. van der Kerk, S. M.; van der Kerk, G. J. M. *J. Organomet. Chem.* 1980, *190*, C11. van der Kerk, S. M.; van Eekeren, A. L. M.; van der Kerk, G. J. M. *Ibid.* 1980, *190*, C8. van der Kerk, S. M.; Roos-Venekamp, J. C.; van Beijnen, A. J. M.; van der Kerk, G. J. M. *Polyhedron* 1983, *2*, 1337. van der Kerk, S. M.; Budzelaar, P. H. M.; van Eekeren, A. L. M.; van der Kerk, G. J. M., *Ibid.* 1984, *3*, 271. van der Kerk, S. M.; Budzelaar, P. H. M.; van der Kerk-van Hoof, A.; van der Kerk, G. J. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 313; *Angew. Chem.* 1984, *96*, 306.

0276-7333/87/2306-1997$01.50/0

Table I. Energies (-au) of CH_3B Isomers and HB

				/6-311G**//6-31G*				
species	point group	3-21G//3-21G	6-31G*//6-31G*	HF	MP2	MP3	MP4	ZPE[a]
			Singlets					
$H-B=CH_2$ (1)	C_{2v}	63.86788 (0)	64.21862 (0)	64.23959	64.46392	64.48595	64.49809	22.6
CH_3-B (2)	C_{3v}	63.83281 (0)	64.18235(0)	64.20458	64.41983	64.44775	64.45941	23.6
$H_2B^{-}=CH^{+}$ (3)	C_{2v}	63.81104 (0)	64.16464 (0)	64.18338	64.39265	64.41979	64.43266	20.3
HB(H)CH (4)	C_s	63.80815	64.16338 (1)	64.18279	64.39813	64.42380	64.43772	19.9
$H_2C(H)B$ (5)	C_s	63.76088	64.11989 (1)	64.14559	64.37514	64.40006	64.41502	20.8
HB	$C_{\infty v}$	24.97680 (0)	25.11826 (0)	25.12744	25.19163	25.20886	25.21498	3.2
			Triplets					
$CHBH_2$ (6)	C_s	63.83486 (0)	64.19326 (0)	64.20847	64.38679	64.41479	64.42318	20.9
CH_2BH (7)	C_s	63.82904 (0)	64.18599 (0)	64.20360	64.38996			22.2
CH_3B (8)	C_s	63.80434	64.15624 (0)	64.17474	64.36678			24.1
HB	$C_{\infty v}$	24.96659	25.10699 (0)	25.11443	25.15732	25.16750	25.17045	4.1

[a] 6-31G* zero-point energies (unscaled) in kcal/mol.

Table II. Relative Energies (kcal/mol) of CBH_3 Isomers (1–3) and Transition Structures (4 and 5)

				/6-311G**//6-31G*				
species		3-21G//3-21G	6-31G*//6-31G*	HF	MP2	MP3	MP4	MP4+ZPE[a]
				Singlets				
$HB=CH_2$	(1)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CH_3B	(2)	22.0	22.8	22.0	27.7	24.0	24.3	25.3
H_2BCH	(3)	35.7	33.9	35.3	44.7	41.5	41.1	39.1
HB(H)CH	(4)	37.5	34.7	35.6	41.3	39.0	37.9	35.5
$H_2C(H)B$	(5)	67.1	62.0	59.0	55.7	53.9	52.1	50.5
				Triplets				
$HCBH_2$	(6)	20.7	15.9	19.5	48.4	44.7	47.0	45.5
$HBCH_2$	(7)	24.4	20.5	22.6	46.4			46.0[b]
CH_3B	(8)	39.9	39.1	40.7	61.0			62.3[b]

[a] ZPE differences have been scaled by a factor of 0.89. [b] MP2 + ZPE values.

products suggested the intermediacy of methylborylene, CH_3–B:, and such formulations have been often employed in the literature (despite the lack of direct evidence for such species). Monovalent boron species are similar to the more familiar carbenes but would be expected from qualitative theoretical considerations to have a singlet ground state. The two vacant π-orbitals on boron should make this species not only reactive but also rearrangement prone. High level theoretical studies on singlet methylcarbene, CH_3–CH, indicate the 1,2-H shift barrier to be vanishingly small and predict that this species is unlikely to be observed experimentally.[4] This raises the similar question with regard to possible existence of CH_3–B:, which we address in this paper.

While it now appears more likely that the products of the reaction of CH_3–BBr_2 with unsaturated compounds occur by additive bromoboration rather than via borylene intermediates,[2,5] monovalent boron compounds might be formed under other conditions and remain of inherent interest. Indeed, Timms has generated BF in the gas phase[6] and West recently has trapped $(C_6H_5)_3$Si–B in a matrix at low temperature.[7] The present theoretical investigation of CH_3–B, the simplest alkyl-substituted borylene, and its potential energy surface should help guide experimentalists in their search for such species. In addition, the nature of species with C=B double bonds, a topic of current experimental investigation,[8] also is addressed.[9,10]

Methods. The Gaussian 82 series of programs and the incorporated basis sets and correlation methods were employed.[11] After preliminary investigations at the lower 3-21G level, all geometries were optimized with the polarized split valence 6-31G* basis. Restricted Hartree–Fock theory (RHF) was used for the singlets and the unrestricted version (UHF) for the triplets. All stationary points were characterized as minima or as transition structures at this level by diagonalizing the Hessian (force constant) matrix. Transition structures have one imaginary frequency, but minima have none. These 6-31G* geometries were employed for single point MP4SDTQ/6-

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(2) Schlögl, R.; Wrackmeyer, B. *Polyhedron* **1985**, *4*, 885 and references cited.

(3) Budzelaar, P. H. M.; van der Kerk, S. M.; Krogh-Jespersen, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 3960.

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(5) Budzelaar, P. H. M., private communication.

(6) (a) Timms, P. L. *Acc. Chem. Res.* **1973**, *6*, 118 and references cited therein. (b) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*, Van Nostrand-Reinhold: New York, **1978**; summarize the literature on a number of BX molecules.

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(10) Comparison may also be made with the results to our study of systems which might have $B\equiv C$ triple bonds. Luke, B. T.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1985**, *122*, 19 and ref 9d.

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311G**//6-31G* ("//" means "at the geometry of") calculations. This triply split basis set is further augmented by p-type polarization functions on hydrogen which are known to lower the energy of transition structures involving hydrogen migration. A modest effect in this direction was found here. Electron correlation corrections were obtained in most cases at the full fourth-order Møller–Plesset level. The final refinement in the relative energies was obtained by including zero point energy (ZPE) corrections. Table I summarizes the absolute and Table II the relative energies of all species investigated. The key geometrical parameters are included on the formulas **1**–**8**; further data can be found in the Carnegie-Mellon Quantum Chemistry Archive.[12]

The Singlet CBH_3 Isomers. The three principal singlet isomers investigated were $CH_2{=}BH$ (**1**),[9] which was isoelectronic with the vinyl cation, methylborylene, $CH_3{-}B$ (**2**), and the BH_2-substituted carbene $H_2B\text{-}CH$ (**3**).[13] The latter can also be formulated as an ylide-like structure, $H_2B^{-}{=}CH^{+}$ (the charges are formal), with a boron–carbon double bond. In addition, two 1,2-shift transition structures **4** and **5** were located.

As can be seen from Table II, the relative stabilities of the isomers **1**–**3** lie in the order given and are relatively insensitive to the level of theory employed. All are local minima at the RHF level, but there is evidence from the post-Hartree–Fock levels that **3** is not a true minimum. Thus, at RHF/6-31G*, the transition structure **4**, for the rearrangement **3** → **1**, has an energy less than 1 kcal/mol higher than **3**. At MP4/6-311G**//6-31G*, **4** becomes 3.2 kcal/mol *lower* than **3**. This suggests that **4** is not a true transition structure and that **3** should rearrange to **1** without activation. At such correlated levels, **3** may be the transition structure for the degenerate exchange of hydrogens in **1**, but this was not checked explicitly. As the π-stabilization in **3** is quite substantial,[9d] the relative instability of this species toward rearrangement to other isomers is noteworthy and reflects the inherent thermochemical instability of carbenes. However, derivatives of **3**, e.g. $(CH_3)_2BCH$, might be observable, since rearrangement barriers of methyl groups in carbenes are generally higher than those for hydrogen migration.[9d]

The isomer of principal interest in the present context, methylborylene (**2**), appears to be a true potential minimum. The activation energy of transition structure **5** for rearrangement into the more stable isomer **1** is relatively large at all levels of theory investigated (Table II). As expected from earlier investigations, larger basis sets and the inclusion of electron correlation decrease this barrier considerably, but our final estimate, 25.0 kcal/mol, is not likely to decrease much further at even higher levels of theory. Hence, under appropriate conditions of generation and observation (e.g. matrix isolation), we predict that singlet $CH_3{-}B$ (**2**) should be a persistent, observable species. Tertiary alkyl-substituted borylenes, e.g. *t*-BuB or 1-adamantyl-B, could be even more stable for the reasons discussed above. It would be of interest to generate such univalent boron intermediates in some unambiguous manner for characterization and study of their chemical reactions.

The Triplet CBH_3 Isomers. The corresponding CBH_3 triplets, **6**–**8**, are substantially less favorable than the singlets (**1**–**3**) and show a different stability order. The BH_2-substituted triplet carbene **6** had the lowest triplet energy and a bent structure. Although triplet $CH_2(^3B_1)$ is 9.1 kcal/mol (expt) more stable than the singlet $(CH_2(^1A_1))$,[14] the excellent π-acceptor substituent BH_2 reverses this order[9d] and triplet $HBCH_2$ (**6**) is indicated to be 6.5 kcal/mol *less* stable than the singlet **3** (Table II). Both carbene electrons are delocalized in **3**, and a linear (C_{2v}) structure results. However, this species is indicated to rearrange spontaneously at higher levels of theory (see above), and it is possible that the energetically less stable triplet **7** might be the only $HBCH_2$ form observable experimentally.

The other two triplet isomers are much less favorable than their singlet counterparts. For $HBCH_2$, the energy difference is 46.0 kcal/mol (**1** vs. **7**) and for CH_3B, the energy difference 37.2 kcal/mol (**2** vs. **8**, Table II). Indeed, with the exception of the transition structure **5**, all stationary points found on the singlet potential energy surface lie below the three minima **6**–**8** on the triplet surface.

Comparison of Methylborylene with Borylene. The singlet and triplet states of methylborylene may be compared with those of the unsubstituted borylene molecules BH, which also has a singlet ground state $(^1\Sigma^+)$.[15] For diatomic BH, the relative energy of the excited triplet state $(^3\Pi)$ has not been found experimentally; the highest level theoretical study[15] gives 31.3 kcal/mol (31.8 kcal/mol after correction for zero-point vibration). The BH singlet has two vacant orbitals on boron and is expected to be stabilized more by π-donor substituents than is the BH triplet, with a singly occupied pπ orbital on boron. BF is a case in point, the $^1\Sigma^+$ state being 88.3 kcal/mol below the $^3\Pi$ state.[6b] Methyl group hyperconjugation is less effective than lone pair π-donation, but nevertheless, the effect persists. Thus the energy of the isogyric reaction (eq 1) is −11.8 kcal/mol at the MP2/6-311G**//6-31G*

$$CH_3B(^3A'') + BH(^1\Sigma^+) \rightarrow CH_3B(^1A_1) + BH(^3\Pi) \quad -11.8\ \text{kcal/mol} \quad (1)$$

+ ZPE level. This means that the singlet–triplet separation in methylborylene is 11.8 kcal/mol higher than in borylene. Using best (T-S) value for BH, the corresponding value of CH_3B estimated to be 43.6 kcal/mol. A greater stabilizing effect of the CH_3 group in $CH_3B(^1A_1)$ relative to that in CH_3BH_2 (which has only one vacant p orbital on boron) is shown by eq 2.

$$CH_3BH_2 + BH(^1\Sigma^+) \rightarrow CH_3B(^1A_1) + BH_3 \quad -9.0\ \text{kcal/mol (MP4/6-31G*/3-21G)} \quad (2)$$

Geometries. The shortest C-B bond determined experimentally (in a $R_2BCNR'_2$ derivative by Nöth and Glaser)[8] has a length of 1.422 (3) Å. However, the electron-donating nitrogen and the other substituents should lead to some elongation over the value calculated (6-31G*) for the C=B double bond in **1**, 1.377 Å (Figure 1). The ylide-like carbene $HC^{+}{=}B^{-}H_2$ (**3**) also has an essentially double bond (1.404 Å), as does the transition structure **4** (1.381 Å). The 6-31G* calculated single C–B bond in CH_3BH_2, 1.574 Å, serves as a reference. Only a modest shortening (0.010 Å) due to double hyperconjugation of the methyl groups with the two vacant boron p orbitals is found in $CH_3{-}B$, **2**. The triplet carbene **6** has one π-electron, and the C–B bond (1.523 Å) is between single and double in length. The transition structure **5** for the re-

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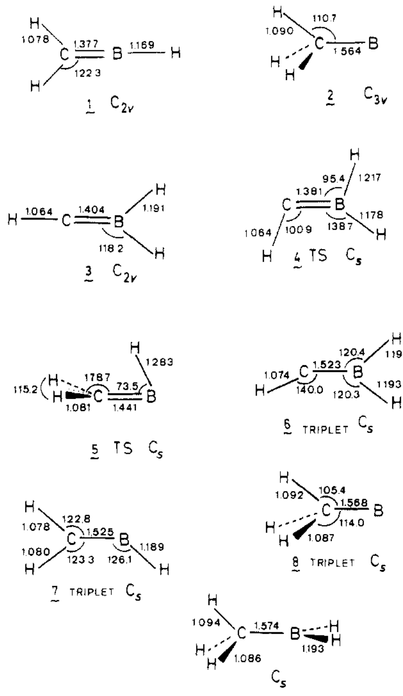

Figure 1. 6-31G* structures of CBH_3 isomers.

arrangement of 2 into 1 has a bridging hydrogen and an intermediate C–B length. The other geometrical data given in Figure 1 (XH bond lengths and angles) reflect the expected effects of hybridization and electronic interactions.

Further Comparisons. Like singlet carbenes, borylenes have both lone pair and empty acceptor orbitals and should exhibit both nucleophilic and electrophilic behavior. Correlated cycloaddition to multiple bonds as well as reactions with both cases and acids is expected. The behavior of protonated methylborylene CH_3–BH^+ (which we have investigated theoretically)[16] contrasts with that of the isoelectronic 2. CH_3–BH^+ is considerably more stable (37.9 kcal/mol at MP4/6-31G*+ZPE) than the isomer $CH_2BH_2^+$, which corresponds to protonated 1. However, $CH_2BH_2^+$ has perpendicular C_{2v} symmetry and lacks the C=B double bond in 1.

Thus, borylenes should be stabilized as complexes with Lewis acids. In addition, π-donor substituents with two sets of electron lone pairs are especially effective, e.g. F in BF ($D_0° = 180$ kcal/mol)[6d] and especially O^- in BO^-, which has the very large electron affinity of 3.12 eV.[6b] We will report the results of a calculational survey of substituted borylenes subsequently.[17]

Postscript. Very recently, Jeong and Klabunde have reported a matrix study[18] that included the reaction of boron atoms with methane. The presence of H_3C–B species was suggested. The spectral lines observed are compared in Table III with those calculated for 2 and its rearrangement product 1. No definite agreement is apparent.

The C=B bond length in a *tetracoordinate* anion, $(mesityl)_2B$=CH_2^-, is 1.444 (8) Å by X-ray analysis,[19] but tricoordinate distances are expected to be shorter.

Table III. Frequencies of BCH_3 Species (cm^{-1})

CH_3—B (2)^a	CH_2=BH (1)^a	expt^b
2877 (e)	3010 (b_2)	2500
2813 (a_1)	2952 (a_1)	2134
1390 (e)	2649 (a_1)	2051
1297 (a_1)	1457 (a_1)	2027
865 (a_1)	1248 (a_1)	2007
590 (e)	880 (b_2)	971
	770 (b_1)	909
	652 (b_1)	894
	452 (b_2)	823

^{a} 6-31G* harmonic frequencies, scaled by 0.89. ^{b} Values given in ref 18. Those near 2000 cm^{-1} are ascribed to "δ_{BH}-bridged" vibrations. See text.

Conclusions. The most important conclusion of this work is that methylborylene is a local minimum on the potential surface with a substantial barrier (25.0 kcal/mol) to rearrangement. Being stabilized by π-donation from the methyl group, the singlet state is far below the triplet (by 43.6 kcal/mol).

Acknowledgment. The research was supported at Pittsburgh by the National Science Foundation (Grant CHE-8409405) and at Erlangen by the Fonds der Chemischen Industrie. J.A.P. is indebted to the Alexander von Humboldt Foundation for a Senior Fellowship. We thank P. Budzelaar for helpful suggestions and H. Nöth for information prior to publication.

Registry No. 1, 56125-75-8; 2, 62785-41-5; 3, 78570-06-6; 4, 13766-26-2.

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Formation and Characterization of $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$, a Dianionic η^6-Arene-Substituted Carbonylmetalate

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Received June 18, 1987

Summary: Naphthalenide reduction of $[Cr(\eta\text{-}C_6H_6)(CO)_2(py)]$ (**1**) (py = pyridine) gives $[Cr(\eta\text{-}C_6H_6)(CO)_2]^{2-}$ (**3**), which reacts with Ph_3SnCl to give $[Cr(\eta\text{-}C_6H_6)(CO)_2SnPh_3]^-$ (1 equiv) or $[Cr(\eta\text{-}C_6H_6)(CO)_2(SnPh_3)_2]$ (**5**) (excess). Addition of NH_4PF_6 (1 equiv) to **3** gives $[Cr(\eta\text{-}C_6H_6)(CO)_2H]^-$ (**6**), and excess NH_4PF_6 gives $[Cr(\eta\text{-}C_6H_6)(CO)_2(NH_3)]$ (**8**) and H_2. Anion **6** reacts with Ph_3SnCl to give a 1:1 mixture of **5** and **8**.

Mononuclear homoleptic carbonylmetalates can be readily prepared for most transition metals, including group 5,[3] 6,[4] 7,[5] 8,[6] and 9[5a,b,7] metals in low (−1 or −2)

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