these highly delocalized covalent compounds, we do so here only for the sake of simplicity. In terms of an MO model we are arguing that the make up of the filled bonding orbitals is mainly ligand in character. Therefore, in the resulting complexes the effective charge on the metal is high.

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bonding found in neutral trigonal prismatic complexes and leading to octahedral geometry for the 2- and 3- complexes. We wish to point out that Gray's21 scheme can equally well accommodate the experimental results. The maleonitrile dithiolate ligand, as a result of its stable orbitals, will render the 4e' MO more ligand in character and as a result addition of two electrons into the $3a'$ $\overline{M}O$, which is mainly metal in character, can still result in a higher effective charge on Mo in keeping with the PE result. The change in geometry is also readily explained; addition of electrons to the 3a' orbital, which is antibonding with respect to the metal ligand (π_h) overlap, and the increase in ligand character of the 4e' orbital both tend to reduce the delocalized bonding between the metal and dithiol and consequently disfavor the trigonal prismatic geometry. Indeed, it will be shown further in the discussion that we believe this delocalized bonding to be primarily responsible for the stabilization of the trigonal prism.

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Organoactinides and Organolanthanides. XII. Bimetallic Tris(cyclopentadienyl)uranium Derivatives with Uranium–Carbon σ Bonds

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New σ -bonded organouranium complexes of the type Cp3U-R (Cp = η ⁵-C₅H₅; R = acetylide, ferrocenyl) and (Cp₃U)₂-R $(R = \text{ferrocentyl}, p\text{-phenyl})$ have been prepared from Cp₃U–Cl and the respective RLi, RNa, or RLi₂ reagents in THF. The ferrocenyl complexes are the first σ -bonded organoactinide compounds where the R group is an organometallic moiety and the (Cp3U)z-R complexes are the only organometallics known to contain two organoactinide moieties bound to the same R group. Infrared and proton nmr spectra support the presence of the R groups as being σ bonded. A mechanism based on large contact effects is used to explain the large isotropic shifts in the nmr spectra. All of the complexes have marked thermal stability and a mass spectrum of the Cp3U-ferrocene derivative is reported. Magnetic susceptibility studies at various temperatures indicate enhanced spin-spin interactions present in the $(Cp_3U)_2-R$ complexes which are absent in their Cp3U-R analogs. Other differences between the Cp3U-R complexes and their "dimeric" analogs are noted.

Within the past few years, the organometallic chemistry of the actinide elements (especially uranium) has received renewed attention.3 Emphasis has been on covalent bonding and the role of the 5f electrons in bonding. Streitwieser, *et al.,4* have presented evidence for a covalent π bond involving the Sf electrons in "uranocene," (CsHs)zU. However, it has only been relatively recently that compounds containing σ -bonded ligands have been prepared and studied. These new types of σ -bonded organoactinide complexes are of the type $(\eta^5$ - C_5H_5)3U-R⁵ and $[(\eta^5-C_5H_5)$ 3U]₂-R₁⁶ where R is an alkynyl, aryl, alkyl, or organometallic ligand. It is becoming clear that these σ -bonded organoactinide compounds will become a wide and varied area of research, especially with regard to covalency^{7,8} and 5f electron involvement in the bonding. With respect to our continuing research in this new area, we wish to report the preparation and properties of several new *u*bonded derivatives.

All reactions and operations were performed using Schlenk techniques or in an inert-atmosphere drybox using dried oxygen-free argon or helium. Tetrahydrofuran (THF) was dried and freed of oxygen by distilling under argon from blue sodium-benzophenone. Other solvents were degassed prior to use and distilled under argon from finely divided lithium aluminum hydride. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Melting points were determined in sealed argon-filled capillaries and are uncorrected.

 $Tris(\eta^5$ -cyclopentadienyl) (acetylenyl) uranium. Into a centrifuge Schlenk tube were placed 2.35 g (5.0 mmol) of $(\eta^5$ -C₅H₅)₃U–Cl⁹ and 0.26 **g** (5.4 mmol) of ethynylsodium.10 Approximately 80 ml of THF was transferred into the tube and the resulting suspension was allowed to stir overnight at room temperature. During this time, the solution changed from dark red-brown to dark green-brown. After centri-

fugation, the solution was transferred into a large Schlenk tube and the THF was removed by distillation *in vacuo* leaving a dark green-brown solid; yield \sim 95%. One gram of this material was continuously extracted with 50 ml of pentane for 10 hr, leaving a dark red-brown residue on the frit. The resulting pentane suspension was centrifuged and the bright yellow-green product was washed once with 25 ml of pentane and dried *in vacuo* at room temperature to yield $0.78 \text{ g of } (\eta^5\text{-}C_5H_5)$ ₃UC \equiv CH. *Anal.* Calcd for C₁₇H₁₆U: C, 44.55; H, 3.52; U, 51.98. Found: C, 43.99; **W,** 3.65; U, 51.93.

Experimental Section
away leaving a brown solid which was washed with hexane and dried $\text{Tris}(\eta^5$ -cyclopentadienyl) (ferrocenyl) uranium. Into a centrifuge Schlenk tube were placed 0.87 g (4.5 mmol) of ferrocenyllithium¹¹ and 2.10 g (4.5 mmol) of $(\eta^5$ -C₅H₅)₃U–Cl. Approximately 60 ml of THF was cooled to -78° and transferred onto the solids. After stirring at -78 ° for 1 hr, all of the insoluble material had dissolved and the solution, intensely red, was allowed to warm gradually to room temperature and to stir overnight. The THF was removed *in vacuo* and the brown solid dried as before. The solid was then placed in a Schlenk-Soxhlet extractor equipped with a frit and continuously extracted with hexane for 18 hr. At this time, the extraction being complete, the solution was centrifuged and the hexane transferred leaving 2.1 g (75%) of (η⁵-C₅H₅)3U-(C₅H₄)Fe(C₅H₅). *Anal.* Calcd for CzjH24FeU: C, 48.56; H, 3.90; Fe, 9.03; U, 38.49. Found: C, **47.56;** H, 5.21; Fe, 8.52: U, 38.13.

1,1'-Bis[tris(n^5 **-cyclopentadienyl)uranium]ferrocene.** Into a centrifuge Schlenk tube were weighed 1.95 g (4.16 mmol) of *(q5-* CsHs)3U-Cl and 0.66 g (2.10 mmol) of $(\eta^5-\text{C}_5\text{H}_4\text{Li})_2\text{Fe-}\text{C}_6\text{H}_16\text{N}_2$.¹² Approximately 60 ml of THF, cooled to -78 °, was transferred onto the solids and the resulting suspension was allowed to stir with gradual warming. At -50° , all of the solid had dissolved and the solution was then warmed to between -20 and -30° . Stirring was maintained for **4** hr during which time a voluminous green precipitate appeared in solution. At this point the tube was warmed to room temperature and centrifuged, and the THF was transferred off. The green solid was washed three times with 20-ml portions of THF and then dried *in vacuo.* It was further purified by continuous extraction with THF

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to yield 1.25 g (60%) of $[(\eta^5{\text{-}}C_5H_5)3U]_2(C_5H_4)_2$ Fe. *Anal.* Calcd for C4oH3sFeU2: C, 45.73; H, 3.64; Fe, 5.32; U, 45.31. Found: C, 45.52; H, 3.70; Fe, 4.97; U, 45.52.

p-Bis[tris(~5-cyclopentadienyl)uranium]benzene. Into a 200-ml Schlenk tube were placed 0.47 g (2.0 mmol) of sublimed *p*dibromobenzene and \sim 0.28 g (40 mmol, a tenfold excess) of lithium metal in the form of small chunks; the lithium metal had been melted and allowed to cool and the clean metal core was used. Approximately 50 ml of THF was cooled to -78° and transferred into the Schlenk tube, **2** drops of n-butyl bromide was added, and the mixture was stirred for 2 hr at -30° during which a red color developed. The mixture was cooled to -78° and filtered to remove excess lithium metal into a centrifuge Schlenk tube containing 1.85 g (4.0 mmol) of $(\eta^5$ -C₅H₅)₃U–Cl. The resulting solution was allowed to warm to room temperature and stirred for 1 hr, during which time glistening red-orange platelets precipitated from the red-brown solution. The suspension was then centrifuged, the solution decanted, and the bright red-orange solid washed twice with 20-ml portions of THF and dried *in vacuo* at room temperature to yield 0.45 g (25%) of $p-[n^5 C₅H₅$)3U]₂C₆H₄. Further purification was attained by continuous extraction into THF as previously described. *Anal.* Calcd for C₃₆H₃₄U₂: C, 45.87; H, 3.64; U, 50.49. Found: C, 45.54; H, 3.66; U, 50.78.

Attempts to Prepare Bis[tris(η^5 -cyclopentadienyl)uranium]acetylide. Several methods were attempted, most of which involved trying to displace the acetylenic proton of $(\eta^5$ -C₅H₅)₃UC=CH.

A. With NaH. A 460-mg (0.1-mmol) amount of $(\eta^5 C_5H_5$)3UC $=$ CH and 55 mg (1.1 mmol) of NaH (50% oil dispersion) were placed in a small Schlenk tube and \sim 10 ml of THF, cooled to -78° , was added. The solution was allowed to warm to room temperature with stirring and bubbles were observed to come out of solution, which turned red-brown. The THF was removed *in vacuo* and the solid extracted with pentane. During the extraction, a green precipitate appeared in the pentane which was identified as starting material. The residue remaining on the frit was extracted with THF but the product isolated from this was found to be devoid of a $C=C$ linkage.

B. With *n*-Butyllithium. A 1.83-g (4-mmol) sample of $(n^5 - n^2)$ C_5H_5)3UC \equiv CH was dissolved in 50 ml of THF. The resulting solution was cooled to -78' and 9.6 ml of 0.42 *M* n-butyllithium in hexane was added, causing the solution to become deep red-brown immediately. The solution was allowed to come to room temperature, the THF removed, and the solid extracted with pentane as before. Beautiful red crystals formed in the pentane, which were identified as $(\eta^5$ -C₅H₅)₃U(C₄H₉).^{5b} No other uranium species could be isolated and no evidence for a $C=$ C linkage could be found.

C. Lithium Carbide. $(n^5-C_5H_5)$ ₃U–Cl and Li₂C₂ were allowed to stir in THF at room temperature for several days but no reaction occurred.

Physical Measurements. Proton nmr spectra of the complexes were recorded at room temperature on Varian T-60 and HA-100 spectrometers. Spectra were obtained in THF and benzene solutions.

Infrared spectra in the 4000-625 cm-1 region were recorded with a Beckman IR-8 spectrophotometer. Samples were prepared as Nujol and Fluorolube mulls and examined between NaCl plates.

Mass spectra were measured at low ionizing voltage and samples were studied by the direct-inlet method.

Magnetic susceptibilities were done by the Faraday method using Hg[Co(SCN)4] as a standard.

Results

In the course of our studies, the following complexes were prepared: $(n^5-C_5H_5)$ 3UC \equiv CH (1) , $(n^5-C_5H_5)$ 3U (C_5H_4) - $Fe(C_5H_5)$ **(2),** $(\eta^5-C_5H_5)$ 3U(C₅H₄)Fe(C₅H₄)U($\eta^5-C_5H_5$)3 **(3),** and $(\eta^5{\text -}C_5H_5)3U(p{\text -}C_6H_4)U(\eta^5{\text -}C_5H_5)3$ (4). All of the compounds studied are sensitive to oxygen and moisture. Compounds **1** and **2** have properties similar to other Cp3U-R $(Cp = \eta^5 - C_5H_5)$ derivatives in terms of solubilities and decomposition products. However, as we reported in an earlier communication,6 **2** and **3** represent the only known examples of Cp3U-R type complexes where R is an organometallic moiety. Also, **3** and **4** are the only organoactinide complexes which contain two actinides "bridged" by (attached to) the communication, σ 2 and 3 represent the on
of Cp₃U–R type complexes where R is
moiety. Also, 3 and 4 are the only organo
which contain two actinides "bridged" by
same ligand.
It was of interest to us to study the beha

It was of interest to us to study the behavior of the "dimers"

(3 and **4)** in comparison to their "monomer" analogs **2** and $(\eta^5$ -C₅H₅)₃U–C₆H₅⁵ (5). In this context, we also attempted to prepare [(Cp3U)2](C=C), *6,* but are so far unsuccessful. We wanted to study the effects of having two metals on the same ligand *vs.* one and especially how the 5f electrons would be affected.

It should be mentioned at this point that $\exists C = C$: and

are isoelectronic with $N=N$ and

respectively. Taube has studied the compounds (NH_3) ₅OsN \equiv NOs (NH_3) ₅ and

$$
(NH_3)_5 RuN \overbrace{\bigcirc} NHu(NH_3)_5
$$

and found that there are electronic metal-metal interactions across the ligand systems.^{13,14} In this context, we wanted to prepare analogous f transition metal complexes of isoelectronic ligands similar to Taube's d transition metal complexes. We then anticipated examination of these compounds for f-f interactions between the metals across the ligand systems and information about the extent of f-electron participation in the bonding.

Synthesis. The new organoactinide complexes were prepared according to reactions 1-3. The complexes were purified by

$$
Cp_3U-Cl + RNa \rightarrow Cp_3U-R + NaCl
$$
 (1)

$$
Cp_3U-Cl + RLi \rightarrow Cp_3U-R + LiCl
$$
 (2)

$$
2Cp_3U - Cl + RLi_2 \rightarrow (Cp_3U)_2 - R + 2LiCl
$$
\n
$$
3, 4
$$
\n(3)

continuous extraction and all gave satisfactory elemental analyses. In the solid state, all of them appear to be stable indefinitely in an atmosphere of Ar. In benzene and THF solutions, there is only slight decomposition after several weeks. **1** and **2** are highly soluble in THF and fairly soluble in aromatic and hydrocarbon solvents. By contrast, the "dimers" **3** and **4** are virtually insoluble in these solvents, being only very sparingly soluble in THF.

As has been noted earlier,⁵ the thermal stability of these compounds is quite high; all are stable *in vacuo* to at least 180°. The decomposition products of **2** and **3** are ferrocene and a brown intractable solid containing cyclopentadiene and uranium. Thus the mode of decomposition, even in the

ı	2	3	4
3120 w	3145 w	3125 w	3106 m
$3100 \; \text{m}$	3115 m	3106 m	$3020 \; \mathrm{m}$
2062 m, br	3096 m	3096 m	1440 s
1439 s	3086 m	3086 m	$1063 \; m$
1282 w	1437 m	1988 w	1058 m
1026 s, sh	1370 m	1684 w	1012 vs
1012 vs	1149 w	1447 s	840 w
896 m	1106 vs	1339 w	805 vs
840 m	1067 w	1143 w	780 vs ≻br
823 m	1052 m	1105s	765 vs.
811 vs. s br	1017 vs	1065 w	
792 vs	1000 m	$1052 \; \mathrm{m}$	
779 vs	816s	1010 vs	
657 vs	$797 s$ r	840 w	
645 vs	778s	816 vs 	
		795 vs br	
		778 vs.	

 a Key: w, weak; m, medium; s, strong; vs, very strong; br, broad.

complexes where R is an organometallic ligand, appears one of proton abstraction by R from a Cp group on uranium to give the free ligand RH (or $RH₂$), which is in agreement with the results obtained by Marks in studies of the decomposition products of tricyclopentadienyluranium alkyls and aryls.5b This is in contrast to d transition metals, whose σ -bonded complexes decompose by the more familiar β elimination or homolytic bond scission.

However, it appears that this unusual result may be peculiar to the Cp₃U system. In our attempts to prepare other σ -bonded derivatives of uranium, we ran the reaction shown in scheme 4. Instead of isolating a σ -bonded complex, we obtained large

$$
(\text{indenyl})_3 \text{U}-\text{Cl}^{15} + \text{Li}(p\text{-} \text{tolyl}) \xrightarrow{\text{THF}} ? \tag{4}
$$

yields of bitolyl and a compound tentatively identified as $(indenyl)$ ₃U^{III};^{16,17} the σ -bonded complex apparently formed and decomposed during the course of the reaction, but decomposition occurred by homolytic bond cleavage with radical coupling rather than proton abstraction.

Thus, it appears that putting substituents on the cyclopentadienyl ligands causes noticeable changes in the stability of the uranium–carbon σ bond.¹⁸⁻²⁰

The infrared spectra of these compounds are consistent with our formulation of them as Cp_3U-R or $(Cp_3U)_2-R$, where R is σ bonded. The major absorptions are listed in Table I. Bands are present in all of the complexes at \sim 3100, 1440, 1010, and 810 cm⁻¹ indicative of an η^5 -cyclopentadienyl moiety.²¹ The C= \equiv C band in 1 appears at 2062 cm⁻¹ and is a broad band of medium intensity similar to the band for the uranium-phenylacetylide derivative (2072 cm⁻¹).^{5a}

The ferrocene complexes, 2 and 3, show a band above 3000 cm^{-1} in addition to those present for the η^5 -cyclopentadienyl group. This arises from the less symmetrical Cp ring on ferrocene to which the uranium is bonded and lends further support to the σ nature of this bond.

In 4, the band at 3020 cm^{-1} is indicative of the C-H stretching for phenyl groups. Also, the band at 840 cm^{-1} arises from the presence of a para-disubstituted phenyl group; in this case, σ bonded to two Cp₃U moieties.

One of the purposes in preparing these compounds was to study them by proton nmr and compare the effects of one Cp3U group per ligand *vs.* two. However, as previously mentioned, we were unable to prepare the "dimer" of the acetylide derivative, and **3** and 4 are so insoluble that no spectra could be obtained. Nmr results for **B** and **2** are listed in Table 11.

As we communicated previously,⁶ a mechanism based on large contact shift contributions rather than pseudocontact effects seems to predominate for **2,** to account for the large upfield shifts. This will also explain the downfield shift for

Table II. Proton Nmr of $Cp_3U-R^{a,b}$

Compd	Signal ^c	Chem shift	Assignment
1 d	s	$-1.53(15)$	Cp, U
	S	14.74(1)	$C = CH$
2^e	Ś	$-1.65(5)$	CpFe
	S	$-2.33(15)$	Cp, U
	m	$-13.46(2)$	β protons on the
			substituted Cp
	m	$-30.59(2)$	α protons

a Pmr data in ppm based on 'IMS occurring at *S* 0; **a** minus sign indicates an upfield shift. \degree All data at 25 \degree . All signals were originally referenced to internal solvent. c Key: s, singlet; m, multiplet. Nmr taken in benzene. ^e Nmr taken in THF. ^{*a*} Pmr data in ppm based on TMS occurring at δ 0
indicates an upfield shift. ^{*b*} All data at 25°. All si
ally referenced to internal solvent. ^{*c*} Key: s, single
d Nmr taken in benzene. ^{*e*} Nmr taken in THF.

Table III. Mass Spectrum of $\text{Cp}_3\text{U}(C_5\text{H}_4)$ $\text{Fe}(C_5\text{H}_5)$ **(2)**

mle	Intens	Assignment	m/e	Intens	Assignment		
618	57.1	M*	303	14.3	CpU^*		
553	85.7	$M - Cp^+$	186	31.0	Cp, Fe^+		
552	100.0	$M - CsHs+$	121	23.8	$CpFe+$		
433	52.3	$Cp3U+$	56	19.0	'Fe ⁺		
368	88.1	Cp, U^*					

the acetylenic proton in **1,** and we believe that the same mechanism is operative here as well. Contact shifts reflect the nature of the unpaired spin density (5f electrons for uranium) through the ligand system and can be related to covalency and bonding. Marks has studied this for other Cp3U-R complexes5b and Streitwieser, *et al.,* have studied this in the "uranocenes."^{4a} Their data indicate that similar effects are responsible for the chemical shifts in the two systems. For our compounds 1 and 2 (as well as the other Cp_3U-R complexes5b), this mechanism is charge transfer from filled ligand MO's to vacant f orbitals on the metal and seems to involve at least some degree of covalency.²²

One of the properties affected on going from one Cp3U group to two is the volatility: **2** sublimes nicely under vacuum at about 180° and *5* will subiime with decomposition, but **3** and **4** are nonvolatile. On heating under reduced pressure, they blacken and decompose.

In fact, **2** is rather volatile (more so than other Gp3U-R complexes) and its mass spectrum was obtained with no difficulty. **A** summary of the major ion fragments is given in Table 111. The parent ion at *m/e* 618 was present as was a peak at 433 corresponding to the Cp₃U⁺ ion. This ion shows successive loss of two cyclopentadienyl groups, but no ion at *m/e* 238 (U+) was observed. The ion at *m/e* 186 is for the ferrocene ion and it shows successive loss of the two rings to give peaks at *m/e* 121 and *56.*

A peak at m/e 552 (M - C₅H₅⁺) was observed. This fragment was also observed in *5* and its deuteriophenyl analog,^{5c} This fragment is further evidence for a mode of decomposition involving intramolecular transfer of H from one of the cyclopentadienyi rings. Also, this fragment at *m/e* 552 was the base peak in the spectrum.

The absence of a peak at m/e 238 (U⁺) is not unusual as other cyclopentadienyl complexes of uranium are without it.23 Like cp3u--cl and **Cp4U,** where the cyclopentadienyl ligands are successively more difficult to remove,²⁴ the Cp₂U⁺ ion in **2** is more intense. The loss of the ferrocene moiety *(m/e* 186) from uranium is not very intense relative to the loss of the first two cyclopentadienyl groups and suggests that the ferrocenyl ligand is not readily dissociated from the uranium and is relatively strongly bound.

The new compounds were studied by magnetic susceptibility at various temperatures to see what effects, if any, two Cp3U groups would have on the ligand *vs.* one. The results for the ferrocene compounds, **2** and **3,** will be discussed, although they are pertinent to the phenyl compounds, 4 and 5, as well.

Several interesting observations were noted as a result of the work performed. The results are plotted in Figure 1. It

is apparent that these compounds **(4** as well)24 continue to display temperature-dependent paramagnetism below 100° K unlike Cp₃U-Cl²⁵ or other Cp₃U-R compounds.⁵ The susceptibility was measured as low as $65^{\circ}K$ and the results seem to indicate that the susceptibility would continue to be temperature dependent even at lower temperatures. Compounds **2-4** differ from the others mentioned in that the former all contain at least two metal atoms (either uranium or iron). The metal atoms may "see" each other in space giving rise to some spin-spin or coupling interaction which is ferromagnetic in nature and hence temperature dependent.26

A second anomaly which we observed is that the susceptibility per uranium, in **3,** is lower than that for **2** (see Figure 1). The reason(s) for this is (are) not immediately obvious. This phenomenon could arisc from increased spin-spin interactions for **3** in the crystal lattice as opposed to **2.** Also, since the molecular symmetries in **2** and **3** are different, increased ligand field distortions conld possibly arise in **3** which would help quench orbital angular momentum and hence reduce the susceptibility.

It was also interesting to us that at lower temperatures the overall susceptibility of **3** was less than **4.** If the geometries of the compounds are as we predict, it is easy to visualize that in **3,** the metals are aligned much better for spin interactions (*i.e.*, the molecular orbitals of the metals extend spatially in a more favorable way toward each other) than in **4** (where the metals are parallel to each other across the phenyl moiety).27 If this is so, there should be enhanced spin interactions in **3** and hence a lower susceptibility, which is the observed case. It thus appears that metal-metal interactions through the organic ligand systems are, at most, not very strong. If this were not the case, one would expect to notice enhanced spin-spin interactions in **4,** more so than **3.** which is not the observed case.

X-Ray crystallographic studies would be invaluable in helping to interpret further the magnetic data. It would also be useful in determining the degree of covalency involved in the σ bond. The bonding mechanism which is proposed for these compounds involves the ligand donating electron density into vacant f orbitals on the uranium. If, for instance, this is the case for **2,** there should be less electron density on the substituted ferrocenyl cyclopentadienyl ring to bond with the iron. This should result in a weaker bond and the resulting ring to iron bond distance should be longer than in free ferrocene or even in the unsubstituted cyclopentadienyl group of the ferrocenyl moiety.

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Registry No. 1, 52827-35-1; **2,** 52827-36-8; **3,** 52827-37-9; **4,** 52827-38-0; $(\eta^5\text{-}CsH_5)$ 3UCl, 1284-81-7; ethynylsodium, 1066-26-8; ferrocenyllithium, 1271-15-4; $(\eta^5$ -C₅H₄Li)₂Fe·C₆H₁₆N₂, 32677-77-3; p-dibromobenzene, 106-37-6.

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- (1) To whom correspondence should be addressed.
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