references to these compounds state that they are inseparable by GC, but we found that they are partially resolved on HPLC, showing a 3:1 trans:cis ratio. The ^{13}C NMR spectrum of the mixture showed, in addition to major signals corresponding to the trans alcohol, minor signals (20–30%) at 77.5 and 13.5 ppm, due to C1 and the methyl group of the cis isomer, shifted upfield as expected from the corresponding signals in the trans isomer at 82.7 and 17.7 ppm. A reaction carried out at 40 °C for 24 h gave the alcohols in 19% yield and the same isomer ratio.

Registry No. 4, 2177-47-1; (±)-**5**, 107298-29-3; (±)-**6**, 73837-42-0; (±)-**7**, 107298-30-6; Cp_2ZrCl_2, 1291-32-3; styrene, 100-42-5; 2-phenylpropene, 300-57-2; 1-phenylpropene, 637-50-3; 3-phenylpropene, 25013-15-4; 1-methoxy-4-(1-propenyl)benzene, 104-46-1; 1-methoxy-4-(methylethenyl)benzene, 1712-69-2; (±)-1-phenylethanol, 13323-81-4; 2-phenylethanol, 60-12-8; acetophenone, 98-86-2; 2-phenylpropanol, 698-87-3; (±)-1-phenylpropanol, 613-86-5; 3-phenylpropanol, 122-97-4; 1-phenyl-1-propanone, 93-55-0; 3-phenylpropyl formate, 104-64-3; (±) 1-(4-methoxyphenyl)propanol, 107298-28-2; 3-(4-methoxyphenyl)propanol, 5406-18-8; 1-(4-methoxyphenyl)-1-propanone, 121-97-1; 1-methoxy-4-propyl benzene, 104-45-0; *trans*-1-phenyl-1-undecene, 107224-27-1; *trans*-1-(4-chlorophenyl)-1-undecene, 107224-28-2; *cis*-1-phenyl-3-undecene, 107224-29-3; (±)-1-phenyl-1-undecanol, 107224-30-6; 11-phenyl-1-undecanol, 61439-50-7; (±)-1-(4-chlorophenyl)-1-undecanol, 107224-31-7; 11-(4-chlorophenyl)-1-undecanol, 107224-32-8; 1-phenylundecane, 6742-54-7; tripheny decyl phosphonium bromide, 32339-43-8; benzaldehyde, 100-52-7; *cis*-1-phenyl-1-undecene, 107224-33-9; 4-chlorobenzaldehyde, 104-88-1; *cis*-1-(4-chlorophenyl)-1-undecene, 107224-34-0; triphenyl octyl phosphonium bromide, 42036-78-2; 3-phenylpropanal, 104-53-0; 2-indanone, 615-13-4.

Electronic Spectroscopy of Iron and Ruthenium Pentamethylcyclopentadienyl–Trimethylphosphine Complexes

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Electronic spectra have been obtained for a series of complexes $(\eta^5\text{-}C_5Me_5)L_2MX$ (M = Ru, Fe; L = PMe_3, PEt_3, CO; X = hydride, halide, alkoxide, alkyl, aryl). The close similarity of the low-energy regions of the spectra of $(\eta^5\text{-}C_5Me_5)(PMe_3)_2RuCH_3$ and ruthenocene suggests that the electronic transitions in the former molecule are derived from 1e, a $\rightarrow$ 2e(dσ^*). These assignments are consistent with spectra measured on complexes in which systematic substitutions of the metal center, dative ligands, and the σ-bonded ligand have been made. Irradiation of $(\eta^5\text{-}C_5Me_5)L_2MX$ leads to L_nX loss, consistent with a photoactive excited state that involves the population of 2e(dσ^*).

Introduction

Little is known about the electronic structures of the excited states of organometallic compounds containing phosphine ligands.[3] The nature of these excited states is particularly significant for those complexes that undergo photoreactions leading to carbon–hydrogen bond activation in hydrocarbons.[4] The primary photochemical process leading to the transient species responsible for C–H activation has been assumed to be either dissociation of a phosphine ligand[5] or, preferentially, photoelimination of H_2,[3a–c] in the case of phosphine–polyhydride complexes.[4a,b,e,f] On the other hand, the previously unprecedented photodissociation of a phosphine ligand rather than H_2 has recently been demonstrated for some polyhydride–phosphine complexes of rhenium, indicating that reductive elimination of dihydrogen[3d,e] is not always the preferred photochemical pathway. Hapticity changes for the metal–cyclopentadienyl bonding mode have also been suggested as an alternative photodissociative process for complexes containing a cyclopentadienyl ligand,[6] e.g. $Cp^*Ir(CO)_2$ (Cp^* = $\eta^5\text{-}C_5Me_5$). Many of the known examples of photochemically induced C–H bond activation involve compounds containing at least one, and, in some cases, all three, of the above ligands. At present, our understanding of their electronic structures and primary photochemical processes is insufficient to discern the relative importance of the various dissociative pathways.

We have observed that alkyl complexes of the type $Cp^*(PMe_3)_2RuR$ thermally activate the C–H bonds of arenes (e.g. eq 1).[7] The mechanism proposed invokes a

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Table I. Observed Electronic Transitions for a Series of Ruthenium and Iron Pentamethylcyclopentadienyl-Phosphine Complexes[a]

compd	V	IV	III	II	I
1. $Cp^*(PMe_3)_2RuH$		37 040 (5200)		31 650 (3300)	*c*
2. $Cp^*(PMe_3)_2RuCH_3$		36 770 (6600)		30 490 (2190)	*c*
3. $Cp^*(PMe_3)_2RuCl$	44 250 sh (11 000)	37 450 (2000)	32 050 (1170)	28 900 (1850)	24 390 sh (520)
4. $Cp^*(PMe_3)_2RuCH_2Si(CH_3)_3$		35 970 (3770)		28 820 (1105)	*c*
5. $Cp^*(PMe_3)_2RuC_6H_5$		36 230 (4540)		28 740 (1590)	*c*
6. $Cp^*(PMe_3)_2RuOC_6H_5$		38 910, 32 360[b] (19 200, 5000)	31 060 sh (3900)	28 650 (2450)	23 640 sh (740)
7. $Cp^*(PMe_3)_2RuBr$		38 170 (7170)	30 030 sh (1300)	28 250 (1710)	23 700 sh (580)
8. $Cp^*(PEt_3)_2RuH$	42 370 sh (13 800)	36 500 (3780)		31 060 (2190)	26 180 sh (500)
9. $Cp^*(PMe_3)(CO)RuCH_2Si(CH_3)_3$		38 170 (4800)		33 110 (2500)	26 880 sh (450)
10. $Cp^*(PMe_3)_2FeCH_3$	42 900 sh (19 020)	30 210 (2360)		22 520 (686)	19 200 sh (225)
11. $Cp^*(PMe_3)_2FeCl$	44 440[d]	31 250	24 210 (213)	19 270 (460)	15 820 (130)

[a] Units are in cm^{-1}. Values in parentheses are extinction coefficients (M^{-1} cm^{-1}); sh = shoulder. [b] These bands probably arise from the OC_6H_5 ligand $\pi-\pi^*$ transitions, masking the weaker transitions observed in this region for the other complexes. [c] Not well enough resolved to determine the transition frequencies. The presence of this band is inferred from the asymmetry of the low-energy flank of band II. [d] A very weak shoulder also appears at 37 040 cm^{-1}.

phosphine loss to yield a 16-electron intermediate, $[Cp^*(PMe_3)RuR]$, capable of C–H bond activation (eq 2–5).

$$Cp^*(PMe_3)_2RuCH_2C(CH_3)_3 + C_6H_6 \rightarrow Cp^*(PMe_3)_2RuC_6H_5 + CH_3C(CH_3)_3 \quad (1)$$

$$Cp^*(PMe_3)_2RuR \rightarrow [Cp^*(PMe_3)RuR] + PMe_3 \quad (2)$$

$$[Cp^*(PMe_3)RuR] + C_6H_6 \rightarrow [Cp^*(PMe_3)Ru(H)(C_6H_5)R] \quad (3)$$

$$[Cp^*(PMe_3)Ru(H)(C_6H_5)R] \rightarrow [Cp^*(PMe_3)Ru(C_6H_5)] + RH \quad (4)$$

$$[Cp^*(PMe_3)RuC_6H_5] + PMe_3 \rightarrow Cp^*(PMe_3)_2RuC_6H_5 \quad (5)$$

Activation of both sp^2 and sp^3 C–H bonds is observed upon photolysis of $Cp^*(PMe_3)_2RuX$ (X = hydride, alkyl, aryl).[5] In light of the thermal chemistry discussed above, a reasonable mechanism would involve photodissociation of PMe_3 as the primary photochemical event, generating an extremely reactive 16-electron intermediate, $[Cp^*(PMe_3)RuX]$ (eq 6). However, the products obtained upon

$$Cp^*(PMe_3)_2RuX \xrightarrow{h\nu} [Cp^*(PMe_3)RuX] + PMe_3 \quad (6)$$

photolysis of $Cp^*(PMe_3)_2RuCH_2Si(CH_3)_3$ could be interpreted in terms of homolysis of the $Ru-CH_2Si(CH_3)_3$ bond.[5] These results prompted a more careful examination of the electronic structure of these complexes.

We report on the electronic spectroscopy of a series d^6 complexes of the general formula Cp^*L_2MX (M = Ru, Fe; L = PMe_3, PEt_3, CO; X = hydride, halide, alkoxide, alkyl, aryl). We have assigned the absorption spectra of this class of complexes on the basis of band intensity and frequency shifts upon systematic substitution of the ligands (X and PMe_3) and metals (Ru and Fe). This approach yields assignments for the absorption bands believed to be responsible for the observed photochemistry.

Experimental Section

The room-temperature electronic absorption spectra of the compounds listed in Table I were measured in rigorously dried and deoxygenated petroleum ether by using a Hewlett-Packard Model 8450A diode array spectrophotometer. To avoid sample degradation due to exposure to air, 1 and 10 mm path length quartz cells, fused to a small flask fitted with a greaseless valve and standard taper joint for attachment to a vacuum line, were used. Solutions of these air-sensitive compounds were prepared in a glovebox under N_2. Solution concentrations ranged from 1.7 × 10^{-4} to 1.3 × 10^{-3} M with an accuracy of ±20%.

The compounds $Cp^*(PMe_3)_2RuX$ (X = H, CH_3, CH_2SiMe_3, Cl, Br) were prepared as reported earlier.[8] Other ruthenium compounds, $Cp^*(PMe_3)_2RuC_6H_5$ and $Cp^*(PEt_3)_2RuH$,[7] $Cp^*(PMe_3)_2RuOC_6H_5$,[9] and $Cp^*(PMe_3)(CO)RuCH_2SiMe_3$,[5] were obtained by straightforward modifications of these procedures. A new synthetic route to the iron analogues, $Cp^*(PMe_3)_2FeX$ (X = H, Cl, CH_3), will be reported shortly.[10]

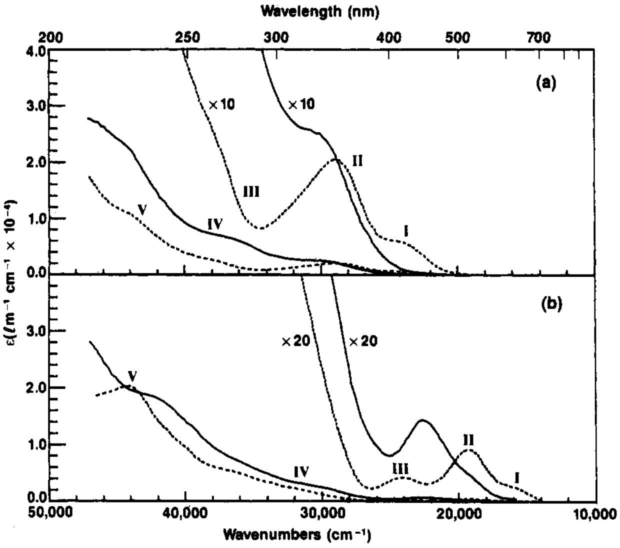

Figure 1. Ultraviolet–visible absorption spectra of the complexes $Cp^*(PMe_3)_2MX$ [X = CH_3 (—), Cl (···)] in petroleum ether solution at 300 K; panel a, M = Ru; panel b, M = Fe.

Results and Discussion

Figure 1 shows the room-temperature electronic absorption spectra of four representative complexes, $Cp^*(PMe_3)_2FeCl$, $Cp^*(PMe_3)_2FeCH_3$, $Cp^*(PMe_3)_2RuCl$, and $Cp^*(PMe_3)_2RuCH_3$. The spectra for the ruthenium complexes possess two major features: (i) a low-energy band (II, ε 1100–3300) at 28 000–33 100 cm^{-1} and (ii) a higher energy band (IV, ε 2000–7200) in the region 36 000–38 200 cm^{-1}. A discernible shoulder (band V, near 43 000 cm^{-1}) is also observed for several complexes. The spectra for the iron complexes show the same three major features. Bands II and IV are both red-shifted by approximately 8000–9500 and ca. 6400 cm^{-1}, respectively, and are 2–4 times weaker than the corresponding ruthenium bands. Weak shoulders (I and III) also appear on the low- and high-energy sides, respectively, of band II and are more pronounced than for the ruthenium complexes.

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Table II. Ligand Field Bands of Cp_2M and $Cp^*M(PMe_3)_2CH_3$ (M = Ru, Fe)

transition[a]	Cp_2Ru	$Cp^*(PMe_3)_2RuCH_3$	Cp_2Fe	$Cp^*(PMe_3)_2FeCH_3$
$^1A_{1g} \rightarrow a^1E_{1g}$	29 500 (120)	30 490 (2190)	21 800 (36)	19 200 (225)
$^1A_{1g} \rightarrow {}^1E_{2g}$	32 500 (160)		24 400 (72)	22 520 (686)
$^1A_{1g} \rightarrow b^1E_{1g}$	36 600 (150)	36 770 (6600)	30 800 (49)	30 210 (2360)

[a] Transition notation refers to D_{5d} Cp_2M molecules; Cp_2M spectral data are from ref 12; band positions are given in cm^{-1}, with ϵ values in parentheses.

Table I lists the transition frequencies and extinction coefficients for each compound, with the observed transitions grouped according to these major features. The data are organized as follows: the first seven complexes, $Cp^*(PMe_3)_2RuX$, for which X is systematically varied, are ordered according to decreasing energy of band II. The spectra of complexes $Cp^*(PEt_3)_2RuH$ (**8**) and $Cp^*(PMe_3)(CO)RuCH_2SiMe_3$ (**9**) show shifts arising from substitution of one or both PMe_3 ligands by PEt_3 or CO, while those of $Cp^*(PMe_3)_2FeCH_3$ (**10**) and $Cp^*(PMe_3)_2FeCl$ (**11**) show the effects of replacing ruthenium with iron (cf. **2** and **5**).

It is observed that the low-energy regions of the spectra of $Cp^*(PMe_3)_2MCH_3$ (M = Fe, Ru) strongly resemble those of the isoelectronic $(\eta^5\text{-}C_5H_5)_2Fe$ and $(\eta^5\text{-}C_5H_5)_2Ru$ species, respectively. There is a strong resemblance in the band positions, as shown by the comparison with ligand field bands of the metallocenes (Table II) and in the intensities (ϵ <2000).[11] This comparison suggests that the well-characterized spectra of the metallocenes[12] could be useful starting points for the discussion and assignment of the observed spectra.

The metallocenes, $(\eta^5\text{-}C_5H_5)_2M$ (M = Ru, Fe), have been investigated, both spectroscopically and theoretically, in great detail. Their ligand field and charge transfer transitions are well understood.[12] Substitution of pentamethylcyclopentadienyl for cyclopentadienyl is expected to red-shift ligand-to-metal charge-transfer bands, but it should not substantially modify interpretation of these metallocene spectra. Substitution of one Cp* ligand by two PMe_3 ligands and a ligand X greatly reduces the symmetry of the chromophore and would be expected to lead to frequency shifts and splittings of the d–d bands. The close resemblance of the $Cp^*(PMe_3)_2MCH_3$ (M = Fe, Ru) spectra with the corresponding metallocene spectra suggests that for this combination of ligands the reduction in symmetry splits and shifts the ligand field transitions to a very small degree. This allows assignment of bands I, II, and IV as d–d transitions. As methyl and PMe_3 are substituted by other ligands, further shifts and possibly additional splitting of these bands would be anticipated; however, their behavior should conform to this assignment. A more detailed discussion of the observed spectral features is presented below.

The intensities of band II in the spectra of the $Cp^*(PMe_3)_2MX$ complexes fall in the range ϵ 400–2000.[11] Furthermore, the transition frequencies decrease in the order of decreasing ligand field strengths, as shown in the following series in which one ligand is systematically varied: H > CH_3 > CH_2SiMe_3, C_6H_5, Cl > OC_6H_5 > Br and CO ≫ PMe_3 > PEt_3. Thus the intensities and systematic frequency shifts are consistent with the assignment of band II and the much weaker, lower energy shoulder (band I), ca 4000 cm^{-1} to the red, as d–d transitions. A very weak band (III) is located to the blue of the ligand field absorption at ca. 31 000 cm^{-1} in complexes containing π-donor ligands. It is readily observed in $Cp^*(PMe_3)_2FeCl$, where it appears as a distinct peak. The low intensity of this band (ϵ <200)[11] again suggests assignment as a ligand field transition. Consistent with this suggestion is the systematic shift to lower energy with decreasing ligand field strength that is more pronounced than for bands I and II.

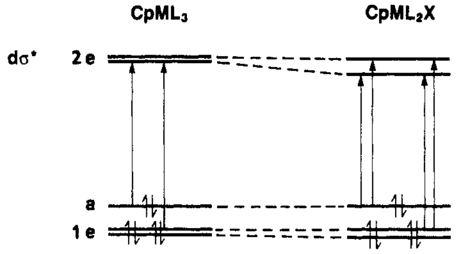

Figure 2. Molecular orbital diagram for d^6 $CpML_3$ and $CpML_2X$ complexes.

Band IV at 36 000 cm^{-1} is not very intense (ϵ <2000),[11] and its position is difficult to locate accurately, since it generally overlaps a very steeply rising absorption edge. Comparison with the ruthenocene spectrum (for M = Ru) suggests a d–d assignment, and the transition frequency shifts (much smaller than for band II) are consistent with this interpretation, except for the π-donor complexes, which show the opposite trend. A possible explanation is that the d–d band does appear in this region but is masked by an overlapping, as yet unassigned band for the π-donor complexes. The band shifts for $Cp^*(PMe_3)_2RuCl$ and $Cp^*(PMe_3)_2FeCl$ complexes are relatively large, nearly 1000 cm^{-1} to the blue of $Cp^*(PMe_3)_2RuCH_3$ and $Cp^*(PMe_3)_2FeCH_3$. For the phenoxide complex, $Cp^*(PMe_3)_2RuOC_6H_5$, interpretation of this region is further complicated by a more intense overlapping band, which is assigned as an intraligand electronic transition of phenoxide.[13]

The observed d–d transitions and photochemistry can be interpreted in terms of the molecular orbital diagram shown in Figure 2. The d-parentage levels are 2e(dσ^*), a, and 1e, with a and 1e split slightly by interactions with the orbitals of Cp and L. The $CpML_3$ level scheme is very similar to that of the metallocenes, since the lone pairs of the ligands that form the three M–L bonds are topologically equivalent to the three π levels of Cp. For the set of ligands L having nearly the same ligand field strength as Cp, the respective complexes will display very similar ligand field spectra. The primary effect of substitution of one by another ligand X is to split the dσ^* orbitals (Figure 2). This splitting will increase, and both levels will shift as the ligand field strengths of L and X become increasingly disparate. Since the a and 1e levels are nearly nonbonding, ligand substitution should affect their energies only to a small extent. Support for this contention comes from photoelectron spectra for the series of d^6 complexes $Cr(CO)_6$, $Mn(CO)_5X$, $CpMn(CO)_3$, and $Cp(CO)_2FeX$, which show no substantial changes in the ionizations as-

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(11) When the background due to the underlying, stronger absorption is subtracted.

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sociated with the metal d orbitals as the symmetry of the complexes is progressively lowered.[14] For the metallocene complexes, transitions from both the a and 1e orbitals to 2e(dσ*) give rise to the three observed bands listed in Table II.[12] The splitting between the two lowest energy bands in the metallocene spectra arises in part from the differences in energy of the a and 1e levels. The energy separation of bands I and II in the spectra listed in Table I probably has a similar origin; in any case, it is not attributable solely to a splitting of 2e(dσ*), although such a splitting may contribute to the increased separation of the bands as the ligand field strengths of X and L diverge.

The proposed electronic structure for the complexes Cp*$(PMe_3)_2$MX, in which the dσ* orbitals possess considerable σ-antibonding character with respect to the M–PMe_3 and M–X bonds, is in accord with the observed photochemistry for Cp*$(PMe_3)_2$RuX (X = H, CH_3, CH_2CMe_3, CH_2SiMe_3), i.e. activation of sp^2 and sp^3 C–H bonds under broad-band UV irradiation ($\lambda_{ex} > 300$ nm). Promotion of an electron to a dσ* orbital would reduce the corresponding M–L or M–X bond strength and lead to photolability of PMe_3 or homolysis of the M–X bond, at least when X is a one-electron σ donor (e.g. hydride or alkyl); see eq 6.

Finally, we note that the use of Cp*$(PMe_3)_2$MX has allowed variation of the metal–ligand environment over a range not usually encompassed in spectroscopic studies of organometallic species. In turn, this has allowed the assignment of the electronic structure of these complexes despite their low symmetry. The analogy to the metallocene spectra is both striking and useful as a tool for assigning spectroscopic features in these complexes. The electronic structure proposed can be correlated to the observed photochemistry of these complexes.

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Synthesis of Carbyne Complexes of Chromium, Molybdenum, and Tungsten by Formal Oxide Abstraction from Acyl Ligands

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Reaction of the acyl metal complexes $[NMe_4][M(C(O)R)(CO)_5]$ (R = C_6H_5, M = Cr, Mo, W; R = CH_3, M = W) with the Lewis acids $COCl_2$, $C_2O_2Cl_2$, $C_2O_2Br_2$, and $ClC(O)OCCl_3$ in CH_2Cl_2 at low temperatures (≤−78 °C) and subsequent warming of the solutions (≤0 °C) lead to clean formation of *trans*-halo(carbyne)tetracarbonylmetal complexes, $[M(CR)(X)(CO)_4]$ (X = Cl, Br). The carbyne complexes $[M(CR)X(CO)_4]$ are transformed into stabilized derivatives $[M(CR)X(CO)_2L_2]$ by the addition of donor ligands (L_2 = $(pyridine)_2$ (py), tetramethylethylenediamine (tmeda), bipyridine (bpy)). The complex $[W(CPh)(O_2CCF_3)(CO)_2(tmeda)]$ is prepared in a similar reaction sequence from $[NMe_4][W(C(O)Ph)(CO)_5]$, $(CF_3CO)_2O$, and tmeda. Reaction of $[NMe_4][W(C(O)Ph)(CO)_5]$ with $C_2O_2Br_2$ and 1 equiv of PPh_3 gives $[W(CPh)Br(CO)_3(PPh_3)]$. The bis(pyridine)-substituted complexes $[W(CPh)Cl(CO)_2(py)_2]$ undergo further substitution reactions with PMe_3 and $Ph_2PCH_2CH_2PPh_2$ (dppe) to give $[W(CPh)Cl(CO)_2(PMe_3)_2]$ and $[W(CPh)Cl(CO)_2(dppe)]$.

Introduction

Metal–carbon triple bonds in transition-metal carbyne, or alkylidyne, complexes are well-established functionalities in organometallic chemistry.[1] Tris(alkoxy)metal alkylidyne complexes of tungsten and molybdenum have been shown to be very active acetylene metathesis catalysts,[2] and *trans*-bromotetracarbonyltungsten carbyne complexes are precursors for active acetylene polymerization catalysts.[3] Several stoichiometric reactions of metal carbyne complexes of potential synthetic use have been discovered, such as the formation of ketenyl ligands by carbonyl–carbyne coupling[4] or the incorporation of carbyne ligands into cyclopentadienyl rings,[5] phenols,[6] olefins,[7] acetylenes,[7] and malonic acid derivatives.[8] Metal–carbon triple bonds have also been demonstrated to undergo formal cycloaddition reactions[9] and have been utilized in the systematic build up of transition-metal cluster structures.[10] Nevertheless, the chemistry of transition-metal carbynes is much less investigated than that of the related transition-metal carbene complexes.[11] One of the reasons for this situation is certainly that metal carbynes are less

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