Transmetalation Reactions from Fischer Carbene Complexes to Late Transition Metals: A DFT Study

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We dedicate this paper to Professor José Barluenga for his outstanding contributions to the development of the applications of organometallic reagents in organic synthesis

Abstract: Transmetalation reactions from chromium(0) Fischer carbene complexes to late-transition-metal complexes (palladium(0), copper(I), and rhodium(I)) have been studied computationally by density functional theory. The computational data were compared with the available experimental data. In this study, the different reaction pathways involving the different metal atoms have been compared with each other in terms of their activation barriers and reaction energies. Although the reaction profiles for the transmetalation reactions to palladium and copper are quite similar, the computed energy values indicate that the process involving palladium as catalyst is more favorable than that involving copper. In contrast to these transformations, which occur via triangular heterobimetallic species, the transmetalation reaction to rhodium leads to a new heterobimetallic species in which a carbonyl ligand is also transferred from the Fischer carbene to the rhodium catalyst. Moreover, the structure and bonding situation of the so far elusive heterobimetallic complexes are briefly discussed.

Keywords: carbenes · catalysis · density functional calculations · reaction mechanisms · transmetalation

Introduction

As the 50th anniversary of the preparation of the first metal–carbene complex by Fischer and Maasböl approaches,[1] the use of these complexes in organic synthesis remains restricted to stoichiometric reactions.[2] On the other hand, stoichiometric metal-to-metal carbene transfer was reported in the early 70s,[3] but this methodology remained undeveloped until our report on the catalytic transfer of a carbene ligand from a Group 6 Fischer carbene complex to a palladium reagent.[4] At that time the mechanism depicted in Scheme 1 was proposed to explain the observed results. Transmetalation of the carbene ligand from complex **1** to the palladium catalyst leads to a new Pd–carbene complex such as **2**, probably through a heterobimetallic intermediate **3** that evolves to **2** by extrusion of the [M(CO)₅] (M=Cr, W) fragment. Subsequent transmetalation from a new molecule of the carbene complex **1** leads to the Pd–biscarbene complexes **4**. Elimination of Pd⁰ leads to the observed dimerization products **5**.

Following this original proposal, the isolation and characterization of pallada–carbene complex **6** by the transmetalation of aminotungsten(0)–carbene complex **7** to [PdPfBr(MeCN)₂] followed by the reaction with PMe₃ was reported.[5] More recently, pallada–biscarbene complexes **8** have been isolated (Scheme 2).[6] Note that neither complex **6** nor complexes **8** evolve to form self-dimerization products.

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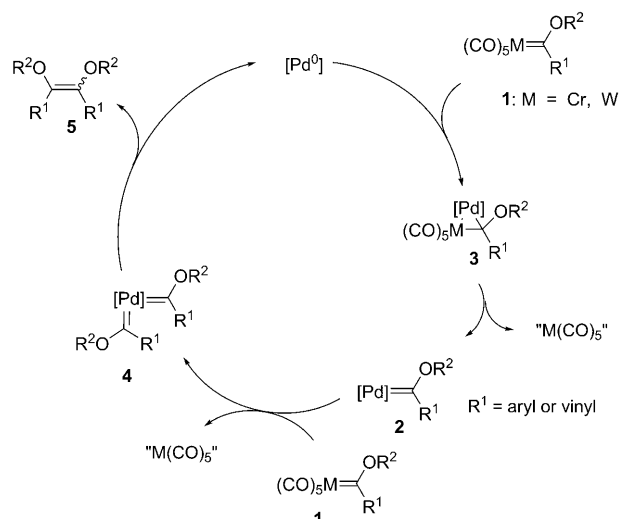
Scheme 1. Proposed transmetalation catalytic cycle from Cr[0]– and W[0]–carbene complexes to Pd[0].[4]

Scheme 2. The isolation of Pd–monocarbene **6** and Pd–biscarbene complexes **8** by transmetalation from W[0]– and Cr[0]–carbene complexes.

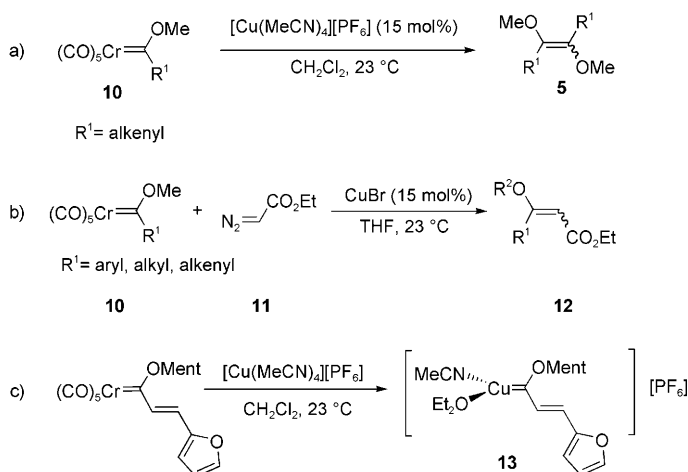Scheme 3. Examples of copper transmetalation and the isolation of Cu–monocarbene complex **13**. Ment = Menthyl.

Furthermore, the self-dimerization of the carbene ligand on the Fischer carbene complexes **10** with [Cu(MeCN)₄]-[PF₆] as a catalyst has been described.[7] CuBr also allowed the efficient and selective cross-coupling of the carbene ligand derived from complexes **10** with those obtained from the decomposition of the diazo compound **11**. Evidence for the formation of late-transition-metal–carbene complexes by a transmetalation reaction was demonstrated by the isolation and full characterization of the corresponding copper–carbene complex **13**, which possesses a bulky stabilizing group that prevents the self-dimerization process (Scheme 3).

The above examples are a few of the many transmetalation processes that have led to new carbene complexes and they exhibit exceedingly different chemical behavior in re-

Abstract in Spanish: *La reacción de transmetalación catalítica desde cromo(0) Fischer carbenos a metales de transición tardía (Pd⁰, Cu^I y Rh^I) se ha estudiado computacionalmente usando DFT. Los resultados computacionales se han comparado con los datos experimentales disponibles. Las barreras y las energías de reacción se han comparado en los caminos de reacción obtenidos para los metales considerados. Mientras que los perfiles de reacción para la transmetalación desde Cr a Pd o Cu son similares, los valores calculados indican que aquellos procesos que implican catalizadores de Pd son más favorables que los que implican Cu. En claro contraste con estas transformaciones, que ocurren a través de especies heterobimetálicas con geometría triangular, la reacción con Rh forma nuevas especies heterobimetálicas en las que se ha transferido un ligando carbonilo desde el complejo de Fischer al catalizador de Rh. Adicionalmente, se discute la estructura y la forma de enlace de éstos complejos heterobimetálicos no aislados hasta este momento.*
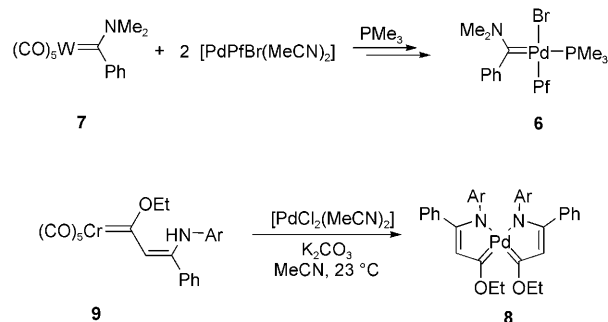
spect of the starting Group 6 metal complex. Moreover, the new carbene complexes may also show an enhanced reactivity with respect to the precursor complex or it may undergo reaction pathways different from the starting carbene complex, which opens the door to the synthesis of new classes of compounds.[8] Although the transmetalation reaction has been employed in the development of new and efficient synthetic methodologies, a detailed mechanistic study has not yet been reported. This is interesting because the isolation of the diverse intermediates discussed above and other experimental evidence point to the correctness of the proposed mechanism.[4] We report herein an extensive theoretical study on the transmetalation reaction from chromium(0)–carbene complexes to palladium, copper, and rhodium catalysts.[2p, 9] Moreover, the structure and bonding situation of the different heterobimetallic intermediates, which lead to mono- and biscarbene complexes of palladium, copper, and rhodium, shall be compared and discussed.

Computational Details

account by using the BP86[11] functional in combination with the standard 6-31G(d) basis set[12] for hydrogen, carbon, oxygen, nitrogen, and phosphorus atoms and the Hay–Wadt small-core effective core potential (ECP) that includes a double-ξ valence basis set[13] for the metal atoms (LanL2DZ keyword). Zero-point vibrational energy (ZPVE) corrections were computed at the BP86/LANL2DZ&6-31G(d) level and were not scaled. Reactants and products were characterized by frequency calculations[14] and have positive definite Hessian matrices. Transition structures (TSs) show only one negative eigenvalue in their diagonalized force constant matrices, and it was confirmed by using the intrinsic reaction coordinate (IRC) method that their associated eigenvectors correspond to the motion along the reaction coordinate under consideration.[15]

Bond orders and donor–acceptor interactions were computed by using the natural bond orbital (NBO) method.[16] The energies associated with these two-electron interactions were computed according to Equation (1), in which $\hat{F}$ is the DFT equivalent of the Fock operator and ϕ and ϕ^* are two filled and unfilled natural bond orbitals with ε_ϕ and ε_{ϕ^*} energies, respectively, and n_f is the occupation number of the filled orbital.

$$\Delta E^{(2)}_{\phi\phi^*} = -n_\phi \frac{\langle \phi^* | \hat{F} | \phi \rangle^2}{\varepsilon_{\phi^*} - \varepsilon_\phi}$$

Geometry optimizations (BP86/6-31G(d)&LanL2DZ) were carried out starting with the *anti* form (an orientation in which the methyl group of the methoxy substituent is directed towards the metal fragment) of the Fischer carbene complex **14** (Scheme 4). This species is the most stable isomer in both the gas phase and in the solid state.[17]
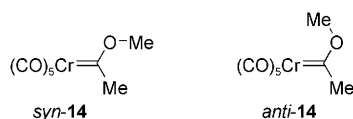
Scheme 4. The *syn* and *anti* forms of chromium(0) (Fischer) carbene complex **14**.

Results and Discussion

Transmetalation to palladium: Transmetalation from Fischer carbene complex **14** to [Pd(PH$_3$)$_4$] was studied first as a model for the experimentally thoroughly studied reaction between the benzyloxycarbenechromium(0) complex **15** and [Pd(PPh$_3$)$_4$], which exclusively produces the self-dimerization product **16** (*E/Z* ratio 1.1:1) without traces of the corresponding β-elimination product **17** (Scheme 5).[4]
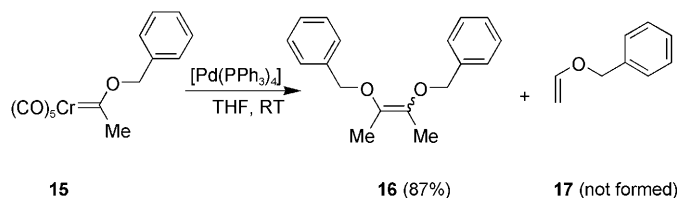
Scheme 5. The [Pd(PPh$_3$)$_4$]-catalyzed self-dimerization of complex **15**.[4]

The transmetalation step that leads to the predicted monocarbene complex **20** from complex **14** in the presence of [Pd(PH$_3$)$_4$] was first studied. No transition-state structure connecting complex **14** and [Pd(PH$_3$)$_4$] with the correspond-

ing heterobimetallic complex **18** by an associative reaction pathway was found. Instead the process starts with the dissociation of one of the catalyst's phosphine ligands to produce the unsaturated species [Pd(PH$_3$)$_3$], which, in the presence of complex **14**, leads to the formation of complex **18** via the saddle point **TS1-Pd** (Scheme 6). The activation barrier for
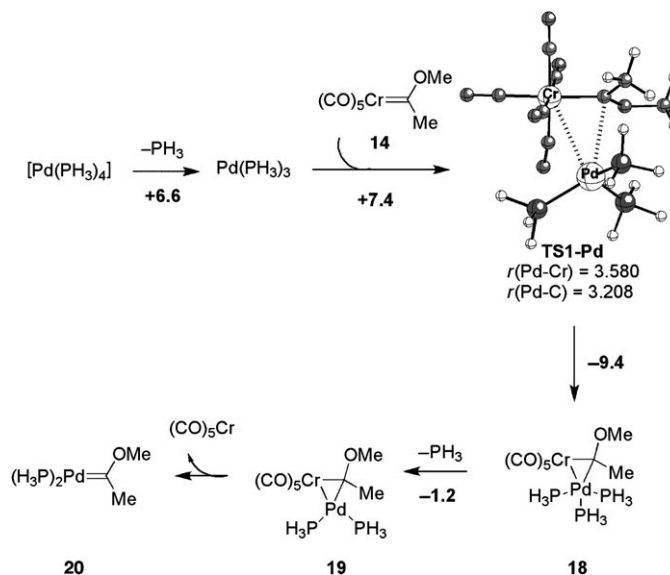
Scheme 6. The first steps in the chromium-to-palladium transmetalation mechanism: The formation of the key Pd–carbene **20**. All structures correspond to fully optimized BP86/LANL2DZ&6-31G(d) geometries. Bond lengths and energies are given in Å and kcal mol^{-1}, respectively. The numbers under the arrows correspond to the relative energies between the corresponding structures. Zero-point vibrational energy corrections have been included [kcal mol^{-1}].

this transformation is only 7.4 kcal mol^{-1} in the gas phase and the reaction energy is −2.0 kcal mol^{-1}. These values are in very good agreement with the mild reaction conditions used experimentally for this transformation. Heterobimetallic complex **18**, with the former carbene ligand as a bridge between the palladium and chromium atoms, evolves to the pallada–carbene complex **20** by the sequential, slightly exothermic dissociation of another PH$_3$ ligand (leading to unsaturated complex **19**) followed by the extrusion of the [(CO)$_5$Cr] fragment. The latter process is likely to be assisted by a solvent molecule in the condensed phase (see below).

The coordinatively unsaturated palladium(0)–carbene complex **20** experiences a second transmetalation reaction with a new molecule of the Fischer carbene complex **14** to yield a new heterobimetallic complex **21** via the transition state **TS2-Pd** (a saddle point associated with the formation of a palladium−carbon bond). The slightly higher barrier of this second transmetalation reaction compared with the conversion of **14** into **18** (activation barrier of 8.6 vs. 7.4 kcal mol^{-1}, respectively) may be attributed to the decreased nucleophilicity of the palladium center in complex **20** due to the more electron-accepting nature of the carbene

ligand. This hypothesis is supported by the second-order perturbation theory of the NBO method, which shows a strong two-electron stabilizing donation from an occupied d atomic orbital of palladium to the π* (C−OMe) molecular orbital of the carbene ligand in complex **20** (associated second-order energy of -14.1 kcal mol^{-1}), which makes the palladium atom less nucleophilic (Figure 1). Evidently, this
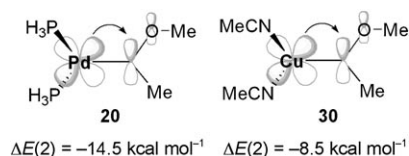

Figure 1. Two-electron interactions and associated second-order perturbational energies in intermediates **20** and **30**.

two-electron donation is not possible in [Pd(PH$_3$)$_3$]. Interestingly, the formation of complex **21** is strongly exothermic (-10.5 kcal mol^{-1}), which is again in good agreement with experimental findings. Furthermore, one of the PH$_3$ ligands in **21** is weakly bonded to the palladium atom (Pd−P bond length of 4.892 Å with a corresponding Wiberg NBO bond order of 0.032). This clearly indicates that this species is a true intermediate complex, which easily evolves to complex **22** in which this PH$_3$ ligand is totally dissociated. Similarly to the first transmetalation step (see Scheme 6), elimination of the [(CO)$_5$Cr] fragment leads to the palladium–biscarbene complex **23** (Scheme 7).
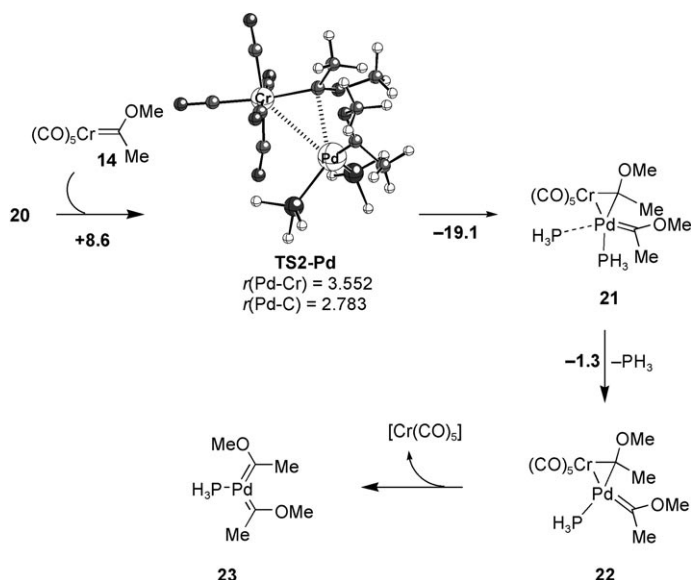
Scheme 7. The formation of pallada–biscarbene complex **23**. See the legend of Scheme 6 for details.

The catalytic cycle that connects the starting chromium(0)–carbene complex **14** with the self-dimerization product **24** ends with the formation of the carbon−carbon bond

in complex **23** and the entry of the catalyst into a new cycle. For simplicity, the formation of the Z isomer is the only one considered (it is reasonable to assume that the E isomer is also formed from **23** by rotation of the Pd−C bond). The addition of one molecule of PH$_3$ saturated the coordination vacancy in **23** to yield the 18-valence-electron complex **25** (Scheme 8). This step is slightly endothermic (reaction
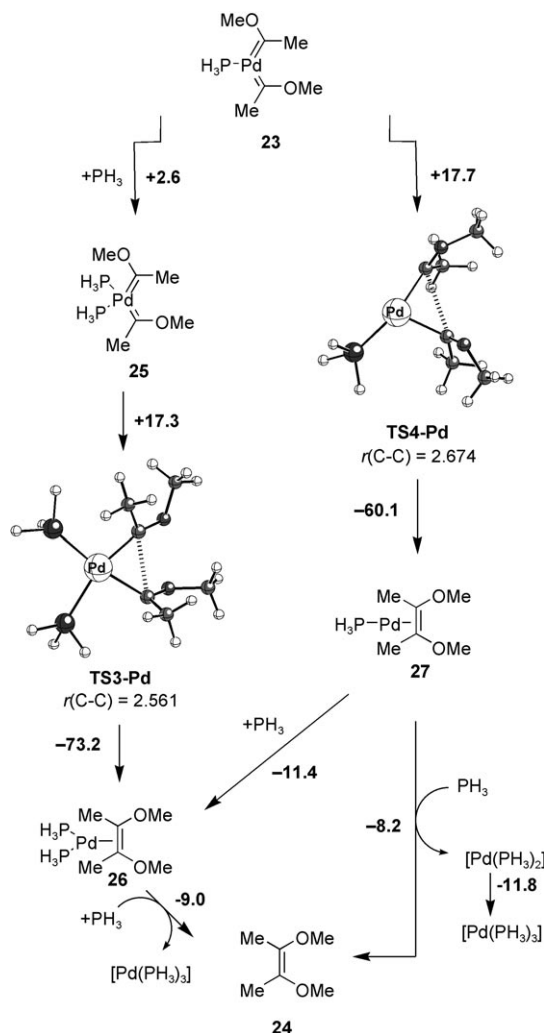

Scheme 8. Final step in the transmetalation reaction from complex **23**. See the legend of Scheme 6 for details.

energy of 2.6 kcal mol^{-1}). From this stationary point, complex **26** is produced via transition state **TS3-Pd**, a saddle point that is associated with C−C bond formation between the two carbene carbon atoms. The activation barrier for this step is 17.3 kcal mol^{-1} and as a consequence it is the bottleneck of the overall catalytic cycle. Nevertheless, the transformation of **25** into **26** is strongly favored by its strong exothermicity (reaction energy of around -56 kcal mol^{-1}). Finally, the coordinated dimerization product in **26** is replaced by a PH$_3$ ligand to close the catalytic cycle and liberate the alkene **24**.

Alternatively, the C–C bond may be formed directly from Pd–biscarbene **23**. In this case, complex **27** is produced via the corresponding transition state **TS4-Pd**. Although the activation barrier for the transformation **23**→**27** (17.7 kcal mol^{-1}) is similar to that for the reaction **25**→**26**, the former pathway is less exothermic (−42.4 kcal mol^{-1}) than the latter. From **27** a new molecule of PH$_3$ can coordinate to the metal center to form **26** or can replace the alkene ligand to form [Pd(PH$_3$)$_2$] and the metal-free olefin **24**. As the ligand interchange is supposed to be fast, we cannot safely discard one reaction pathway in favor of the other on the basis of the computed energies (Scheme 8).

According to the available experimental data[4] there is an additional pathway to be disentangled in this mechanism, namely the possible β-elimination process from pallada–carbene complexes **20**, which produces enol ether **28** depending on the reaction conditions (these compounds are formed normally in the reaction of chromium(0)–carbene complexes with hydrogen atoms α to the carbene carbon atom and [Pd-(OAc)$_2$]/Et$_3$N. Scheme 9 shows the computational results for
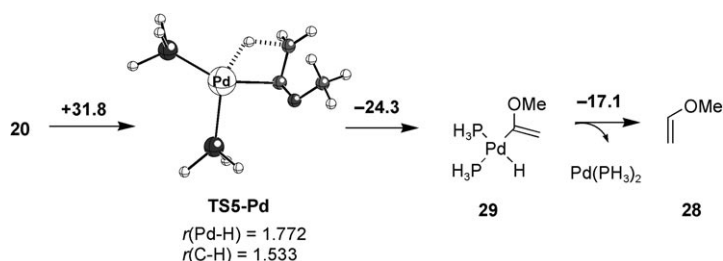
Scheme 9. The β-elimination process in pallada–carbene **20** bearing alkyl substituents. See the legend of Scheme 6 for details.

these competitive processes. The computed activation barrier for the **20**→**29** transformation is 31.8 kcal mol^{-1}, which makes the β-elimination process kinetically unfavorable compared with the transmetalation step **20**→**21** (activation barrier of 8.6 kcal mol^{-1}). Moreover, the β-elimination process is also endothermic (reaction energy of 7.5 kcal mol^{-1}) and therefore it is thermodynamically disfavored. The computed energies are in very good agreement with the nonformation of enol ethers observed experimentally using [Pd-(PPh$_3$)$_4$] as the catalyst for the transmetalation reaction.

Transmetalation to copper: The reaction profile of the reaction of Fischer carbene complex **14** and [Cu(MeCN)$_4$]$^+$ has been computed as the model reaction for the transmetalation from chromium(0) Fischer carbene complexes to copper catalysts (Scheme 3c). The essentials of this pathway are shown in Scheme 10. The calculated reaction profile (BP86/6-31G(d)&LanL2DZ) for the transmetalation reaction to Cu^I is very similar to the corresponding process involving Pd^0. Again, two different transmetalation steps were found, the second one being more difficult and more endothermic (activation barrier of 10.0 kcal mol^{-1} and reaction energy of 5.9 kcal mol^{-1}) than the first one (activation barri-

er of 4.2 kcal mol^{-1} and reaction energy of −1.3 kcal mol^{-1}). Similarly to the palladium reaction, the lower nucleophilicity of the copper(I)–carbene complex **30** compared with [Cu-(MeCN)$_3$]$^+$, due to the exchange of a MeCN ligand for the more electron-accepting carbene ligand, may explain the computed values. In fact, the second-order perturbation theory of the NBO method shows again a strong two-electron stabilizing donation from an occupied d atomic orbital of the copper to the π* (C–OMe) molecular orbital of the carbene ligand in complex **30** (associated second-order energy of −8.5 kcal mol^{-1}) making the copper atom less nucleophilic (Figure 1). The structure of the copper(I)–carbene complex **30** is quite similar to that of carbene **13** determined by X-ray diffraction.[7a] In fact, the computed structure shows a carbene ligand perpendicular to the plane formed by the [Cu(MeCN)$_2$] fragment and with a similar Cu–C bond length (calcd: 1.914 Å, X-ray structure: 1.882 Å).[7a]

Note that complex [(CO)$_5$Cr(MeCN)] was detected by NMR spectroscopy of the crude of the reaction shown in Scheme 3c and its structure was assigned by comparison with an authentic sample.[7a] Therefore, it is very likely that the direct decoordination of one MeCN ligand and the elimination of the pentacarbonylchromium(0) fragment, which directly leads to the transformation of complex **31** into **30**, may be solvent-assisted in view of the lower endothermicity of this process compared with the elimination of MeCN to form **32** and subsequent extrusion of the [Cr(CO)$_5$] fragment. A similar process may be assumed in the transformation of complex **33** into the mononuclear copper(I)–biscarbene complex **34** and, by analogy, in the transmetalation from chromium to palladium discussed above. The evolution of intermediate **34** to the alkene **24** follows similar reaction pathways to those discussed above in the transmetalation from chromium to palladium. Thus, either direct C–C bond formation through **TS4-Cu** to form complex **37** followed by the liberation of the alkene **24** after coordination of a molecule of MeCN or, alternatively, from **35** via **TS3-Cu** (associated again with C–C bond formation) to form complex **36**, which produces the alkene **24** and [Cu(MeCN)$_3$]$^+$. This C–C bond formation step is kinetically demanding (computed activation barrier ca. 22 kcal mol^{-1}) but it is thermodynamically strongly favored (reaction energies of ca. −40 kcal mol^{-1}). Therefore, this process is more difficult from both kinetic and thermodynamic points of view than the analogous evolution of palladium intermediate **23** (Scheme 8), which has a lower activation barrier and reaction energy.

Transmetalation to rhodium: The transmetalation to rhodium(I) complexes[18] was the last process studied. We considered the reaction shown in Scheme 12 as a model reaction of the experimentally studied transformation depicted in Scheme 11, which produces rhodium complexes **39** from Fischer carbene complexes **38**.[18i]

In contrast to the transmetalation from chromium to palladium or copper discussed above, the reaction of chromium(0) Fischer carbene complex **14** and Rh^I complex **40** leads to a new type of heterobimetallic complex **41** through
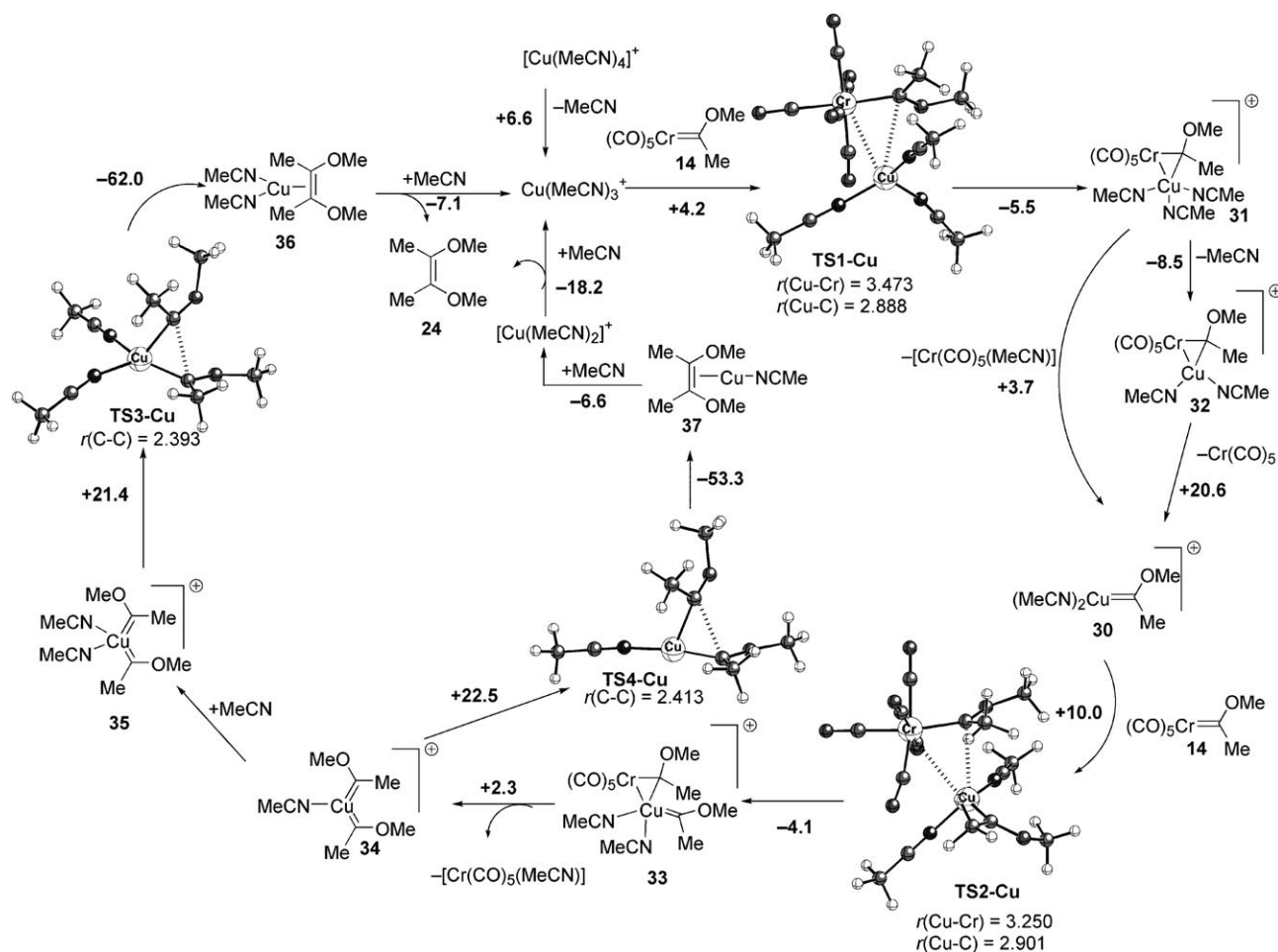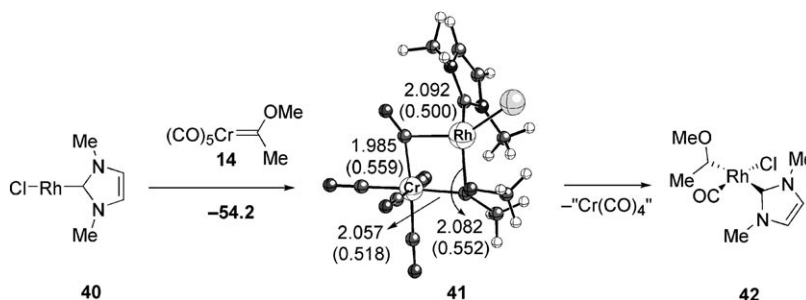
Scheme 10. The full computed mechanism for the transmetalation of chromium(0) Fischer carbene complexes to Cu^I catalysts. All structures correspond to fully optimized BP86/LANL2DZ&6-31G(d) geometries. Bond lengths and energies are given in Å and kcal mol^{-1}, respectively. Numbers over the arrows correspond to the relative energies between the corresponding structures. Zero-point vibrational energy corrections have been included [kcal mol^{-1}].
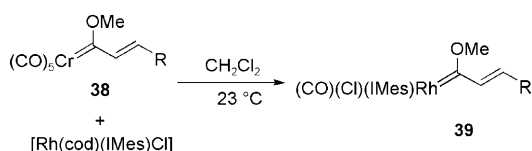
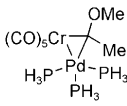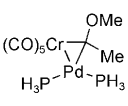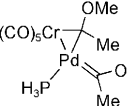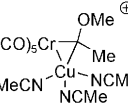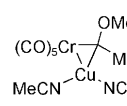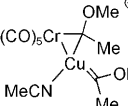Scheme 11. Stoichiometric rhodium transmetalation reaction of Fischer carbene complexes. IMes = N,N'-1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

a strongly exothermic transformation (Scheme 12). Complex **41** has two bridging ligands (one a carbene ligand and one a carbonyl group) tethering the two metal centers.[18d,19] Therefore, and in agreement with experimental findings, transmetalation of the Fischer carbene complexes to rhodium occurs with carbonylation leading to

rhodium–carbene complexes like **42**, which incorporate a carbonyl ligand into their structures. Again, the optimized geometry of **42** fully matches the structure of similar reported Rh^I–carbene complexes characterized by X-ray diffraction (i.e., Rh−C bond length: exp.: 2.011 calcd: 1.983 Å).[18i]

Scheme 12. Transmetalation reaction from Fischer carbene **14** and Rh^I complex **40**. Bond lengths and bond orders (in brackets) are given in Å and a.u., respectively.

Table 1. Selected bond lengths (r(X−Y)), bond orders (B(X−Y) [a.u.], in parentheses), and NBO partial charges for heterobimetallic complexes **18**, **19**, **22**, **31–33**.[a]

	18	19	22	31	32	33
r(Cr−C) [Å]	2.169	2.186	2.203	2.075	2.088	2.132
	(0.446)	(0.448)	(0.419)	(0.584)	(0.577)	(0.520)
r(M−C) [Å]	2.173	2.113	2.098	2.242	2.100	2.111
	(0.406)	(0.445)	(0.463)	(0.223)	(0.263)	(0.296)
r(Cr−M) [Å]	2.798	2.714	2.754	2.593	2.565 2.677	
	(0.079)	(0.096)	(0.083)	(0.073)	(0.081)	(0.067)
q(Cr)	−1.33	−1.34	−1.34	−1.37	−1.37	−1.35
q(M)	0.27	0.24	0.31	0.96	0.93	0.93
q(C)	0.16	0.15	0.11	0.25	0.20	0.14

[a] All data were computed at the BP86/6-31(d)&LanL2DZ level of theory.

Bonding in heterobimetallic intermediates: The structures and bonding situation of the so far elusive Pd–Cr heterobimetallic complexes **18**, **19**, and **22** and the corresponding Cu–Cr analogues **31–33** deserve further analysis. The essential geometric features and NBO partial charges of these species are compiled in Table 1. The AIM method[20] clearly indicates that, as expected, all the species are characterized by the presence of a carbene ligand, which acts as a bridging ligand between the two metal atoms in each complex. Thus, the Laplacian of the electron-density plots of complexes **18** and **31** shows that the electron density of the carbon atom (former carbene carbon atom in Fischer carbene complex **14**) is directed towards the chromium and the palladium or copper atoms (Figure 2).

Strikingly, whereas the palladium complexes have quite similar Cr−C and Pd−C NBO bond orders (ca. 0.45 a.u.), the corresponding NBO bond orders in the analogous copper complexes are rather different (Cr−C bond order of ca. 0.55 a.u. and Cu−C bond order of ca. 0.25 a.u.). This means that the interactions between the ligand and the two metal atoms in palladium complexes **18**, **19**, and **22** are similar, whereas in the corresponding copper complexes the interaction with the chromium moiety is stronger than with the copper fragment. This effect is of course reflected in longer Cr−C bond lengths in the palladium complexes (>2.15 Å) with respect to their copper analogues (ca. 2.1 Å). This is also seen in the Laplacian plot of **31** in which the charge density of the carbon atom is mainly directed towards the chromium atom whereas in **18** it is equally oriented in the direction of both the metal fragments (Figure 2). Moreover, both types of complexes exhibit almost negligible values of the computed Wiberg bond orders (less than 0.1 a.u.) for the M−Cr bond. In addition, a (3,−1) bond critical point between the two metal atoms cannot be found by using the AIM method. Therefore we can conclude that the interaction between the two metal atoms is indeed very weak.

The replacement of a PH$_3$ ligand in **19** by a carbene ligand in **22** results in only slight changes in the structure of

the complex. Thus, the Pd−C(bridge) bond is shortened due to the higher acceptor ability of the palladium moiety in **22** due to the presence of the acceptor carbene ligand. This results in a stronger Pd−C interaction at the expense of a
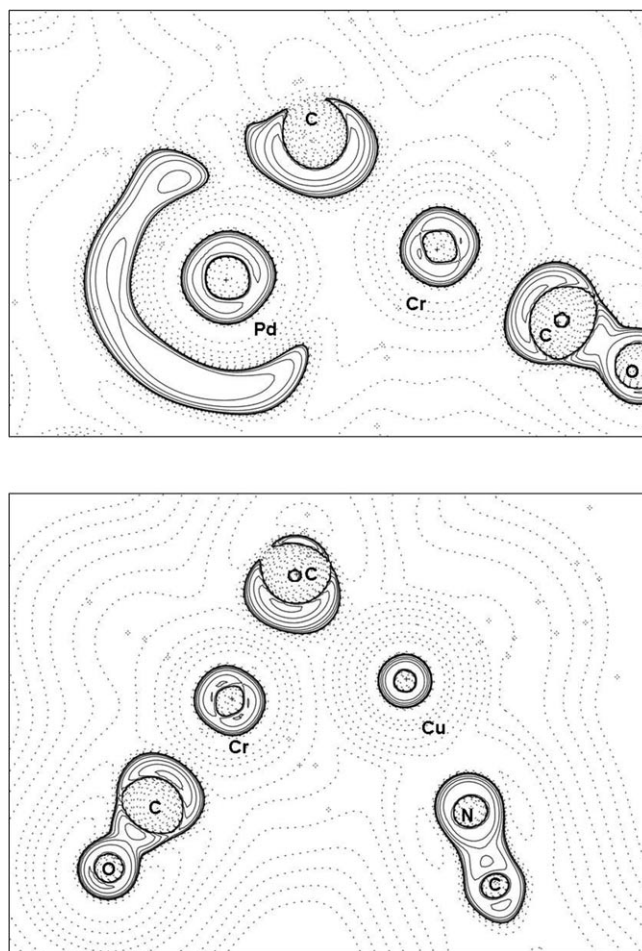

Figure 2. Laplacian $\nabla^2\rho(r)$ plot for complexes (a) **18** and (b) **31** (down). Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$) and dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$).

weaker Cr–C interaction, and this is nicely reflected in the lengthening of the latter bond (from 2.186 Å in **19** to 2.203 Å in **22**). Similar conclusions can be drawn when one compares the copper complexes **32** and **33**, the latter containing a carbene ligand in its structure. Again, a stronger interaction between the bridging ligand and the copper moiety provokes a lengthening of the Cr−C bond length (from 2.088 Å in **32** to 2.132 Å in **33**, Table 1).

To complete this study the double-bridged structure of the rhodium(I) complex **41** was analyzed by both the NBO and AIM methods. The computed M–C Wiberg bond orders are quite similar for all M−C bonds (ca. 0.5 a.u., see Scheme 12), which indicates that the bonding interactions of the two bridging ligands with each of the metal fragments are essentially the same. This is also supported by the Laplacian plot of **41** (Figure 3), which clearly shows that the charge density of both carbon atoms is uniformly oriented towards both metal atoms.
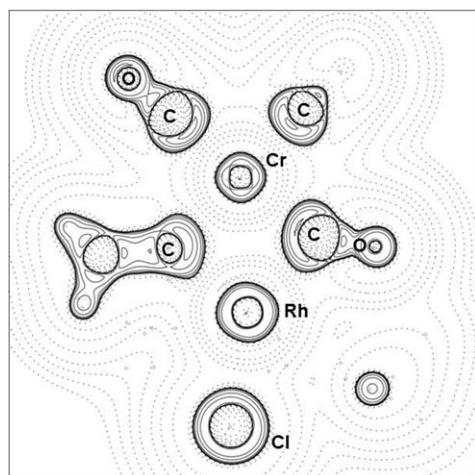

Figure 3. Laplacian $\bigtriangledown^2\rho(r)$ plot of complex **41**. Solid lines indicate areas of charge concentration ($\bigtriangledown^2\rho(r)<0$) and dashed lines show areas of charge depletion ($\bigtriangledown^2\rho(r)>0$).

Conclusion

From the computational study reported in this paper the following conclusions can be drawn: 1) The transmetalation reaction from Fischer carbene complexes to Pd^0 or Cu^I leads to the dimerization of the carbene ligands in metalla–biscarbene complexes. 2) In both cases C−C bond formation is the most difficult step in the overall reaction mechanism although it is thermodynamically strongly favored. 3) Although the reaction profiles of the transmetalation reactions to palladium and copper are quite similar, the computed activation barriers and reaction energies indicate that the process involving palladium as catalyst is more favorable than that involving copper. 4) The transmetalation step leads to triangular heterobimetallic species in which the former carbene ligand acts as a bridging ligand between the two metal atoms. Interestingly, the interaction between the two metal nuclei is rather weak. 5) In contrast to these transformations, the transmetalation reaction to rhodium(I) leads to a new heterobimetallic species in which a carbonyl ligand is also transferred from the Fischer carbene complex to the rhodium catalyst.

Acknowledgements

[1] E. O. Fischer, A. Maasböl, *Angew. Chem.* **1964**, *76*, 645; *Angew. Chem. Int. Ed. Engl.* **1964**, *3*, 580.

[2] For selected reviews on the chemistry and synthetic applications of Fischer carbene complexes, see: a) K. H. Dötz, H. Fischer, P. Hofmann, R. Kreissel, U. Schubert, K. Weiss, *Transition Metal Carbene Complexes*, Verlag Chemie, Deerfield Beach, FL, **1983**; b) K. H. Dötz, *Angew. Chem. Int. Ed. Eng.* **1984**, *23*, 587; c) W. D. Wulff in *Comprehensive Organic Synthesis, Vol. 5* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 1065; d) M. A. Schwindt, J. R. Miller, L. S. Hegedus, *J. Organomet. Chem.* **1991**, *413*, 143; e) H. Rudler, M. Audouin, E. Chelain, B. Denise, R. Goumont, A. Massoud, A. Parlier, A. Pacreau, M. Rudler, R. Yefsah, C. Álvarez, F. Delgado-Reyes, *Chem. Soc. Rev.* **1991**, *20*, 503; f) D. B. Grotjahn, K. H. Dötz, *Synlett* **1991**, 381; g) W. D. Wulff in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, p. 470; h) L. S. Hegedus in *Comprehensive Organometallic Chemistry II, Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, p. 549; i) D. F. Harvey, D. M. Sigano, *Chem. Rev.* **1996**, *96*, 271; j) R. Aumann, H. Nienaber, *Adv. Organomet. Chem.* **1997**, *41*, 163; k) B. Alcaide, L. Casarrubios, G. Domínguez, M. A. Sierra, *Curr. Org. Chem.* **1998**, *2*, 551; l) M. A. Sierra, *Chem. Rev.* **2000**, *100*, 3591; m) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem.* **2000**, *112*, 4124; *Angew. Chem. Int. Ed.* **2000**, *39*, 3964; n) J. Barluenga, J. Flórez, F. J. Fañanás, *J. Organomet. Chem.* **2001**, *624*, 5; o) J. Barluenga, J. Santamaría, M. Tomás, *Chem. Rev.* **2004**, *104*, 2259; p) M. A. Sierra, M. Gómez-Gallego, R. Martínez-Álvarez, *Chem. Eur. J.* **2007**, *13*, 736.

[3] For carbene ligand transfer from molybdenum to iron complexes, see: a) E. O. Fischer, H. J. Beck, *Angew. Chem.* **1970**, *82*, 44; *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 72; b) E. O. Fischer, H. J. Beck, *Chem. Ber.* **1971**, *104*, 3101; c) E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Müller, E. Winkler, *Chem. Ber.* **1972**, *105*, 162; from chromium to tungsten, see: d) C. P. Casey, R. L. Anderson, *J. Chem. Soc. Chem. Commun.* **1975**, 895; from chromium, molybdenum, or tungsten to gold, see: e) R. Aumann, E. O. Fischer, *Chem. Ber.* **1981**, *114*, 1853; f) E. O. Fischer, M. Böck, R. Aumann, *Chem. Ber.* **1983**, *116*, 3618; g) E. O. Fischer, M. Boeck, *Monatsh. Chem.* **1984**, *115*, 1159; from tungsten to manganese, see: h) B. H. Edwards, M. D. Rausch, *J. Organomet. Chem.* **1981**, *210*, 91; the formation of polynuclear complexes resulting from carbene ligand transfer was observed when using platinum, see: i) T. V. Ashworth, J. A. K. Howard, M. Laguna, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1980**, 1593; j) M. Berry, J. A. K. Howard, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1980**, 1601; k) T. V. Ashworth, M. Berry, J. A. K. Howard, M. Laguna, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1980**, 1615.

[4] a) M. A. Sierra, M. J. Mancheño, E. Sáez, J. C. del Amo, *J. Am. Chem. Soc.* **1998**, *120*, 6812; b) M. A. Sierra, J. C. del Amo, M. J. Mancheño, M. Gómez-Gallego, *J. Am. Chem. Soc.* **2001**, *123*, 851

[5] a) A. C. Albéniz, P. Espinet, R. Manrique, A. Pérez-Mateo, *Angew. Chem.* **2002**, *114*, 2469; *Angew. Chem. Int. Ed.* **2002**, *41*, 2363;

b) A. C. Albéniz, P. Espinet, R. Manrique, A. Pérez-Mateo, *Chem. Eur. J.* **2005**, *11*, 1565.

[6] a) M. P. López-Alberca, M. J. Mancheño, I. Fernández, M. Gómez-Gallego, M. A. Sierra, R. Torres, *Org. Lett.* **2007**, *9*, 1757; b) for a recent stoichiometric carbene transfer from chromium to palladium, platinum, and gold, see also: F. Kessler, N. Sznesni, C. Maass, C. Hohberger, B. Weibert, H. Fischer, *J. Organomet. Chem.* **2007**, *692*, 3005.

[7] a) J. Barluenga, L. A. López, O. Löber, M. Tomás, S. García-Granda, C. Álvarez-Rúa, J. Borge, *Angew. Chem.* **2001**, *113*, 3495; *Angew. Chem. Int. Ed.* **2001**, *40*, 3392; b) J. Barluenga, P. Barrio, R. Vicente, L. A. López, M. Tomás, *J. Organomet. Chem.* **2004**, *689*, 3793.

[8] For a survey of the catalytic transmetalation reaction from Group 6 metal (Fischer) carbene complexes to late-transition-metal reagents, see: M. Gómez-Gallego, M. J. Mancheño, M. A. Sierra, *Acc. Chem. Res.* **2005**, *38*, 44.

[9] For selected reports on theoretical studies concerning Fischer carbene complexes, see: a) A. Arrieta, F. P. Cossío, I. Fernández, M. Gómez-Gallego, B. Lecea, M. J. Mancheño, M. A. Sierra, *J. Am. Chem. Soc.* **2000**, *122*, 11509; b) M. A. Sierra, I. Fernández, M. J. Mancheño, M. Gómez-Gallego, M. R. Torres, F. P. Cossío, A. Arrieta, B. Lecea, A. Poveda, J. Jiménez-Barbero, *J. Am. Chem. Soc.* **2003**, *125*, 9572; c) I. Fernández, M. A. Sierra, M. Gómez-Gallego, M. J. Mancheño, F. P. Cossío, *Chem. Eur. J.* **2005**, *11*, 5988; d) G. Frenking, M. Solá, S. F. Vyboishchikov, *J. Organomet. Chem.* **2005**, *690*, 6178, and references therein; e) I. Fernández, M. A. Sierra, F. P. Cossío, *J. Org. Chem.* **2006**, *71*, 6178; f) C. F. Bernasconi, S. Bhattacharya, P. J. Wenzel, M. M. Olmstead, *Organometallics* **2006**, *25*, 4322; g) I. Fernández, F. P. Cossío, M. A. Sierra, *Organometallics* **2007**, *26*, 3010; h) J. Barluenga, F. Andina, F. Aznar, C. Valdés, *Org. Lett.* **2007**, *9*, 4143; i) E. Stander, C. Esterhuysen, J. M. McKenzie, S. Cronje, H. G. Raubenheimer, *Dalton Trans.* **2007**, 5684; j) I. Fernández, M. A. Sierra, F. P. Cossío, *J. Org. Chem.* **2008**, *73*, 2083; k) I. Fernández, M. A. Sierra, M. J. Mancheño, M. Gómez-Gallego, F. P. Cossío, *Eur. J. Inorg. Chem.* **2008**, 2545; l) M. L. Lage, I. Fernández, M. J. Mancheño, M. A. Sierra, *Inorg. Chem.* **2008**, *47*, 5253; for a featured discussion, see: m) M. A. Sierra, I. Fernández, F. P. Cossio, *Chem. Commun.* **2008**, 4671.

[10] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford, CT, **2004**.

[11] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822.

[12] W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, **1986**, p. 76, and references therein.

[13] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[14] J. W. McIver, A. K. Komornicki, *J. Am. Chem. Soc.* **1972**, *94*, 2625.

[15] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

[16] a) J. P. Foster, F. Weinhold, *J. Am. Chem. Soc.* **1980**, *102*, 7211; b) A. E. Reed, F. J. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736; c) A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735; d) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.

[17] a) I. Fernández, F. P. Cossío, A. Arrieta, B. Lecea, M. J. Mancheño, M. A. Sierra, *Organometallics* **2004**, *23*, 1065; b) D. M. Andrada, M. E. Zoloff Michoff, I. Fernández, A. M. Granados, M. A. Sierra, *Organometallics* **2007**, *26*, 5854.

[18] a) I. Göttker-Schnetmann, R. Aumann, *Organometallics* **2001**, *20*, 346; b) I. Göttker-Schnetmann, R. Aumann, O. Kataeva, C. Holst, R. Frölich, *Organometallics* **2001**, *20*, 2889; c) I. Göttker-Schnetmann, R. Aumann, K. Bergander, *Organometallics* **2001**, *20*, 3574; d) J. Barluenga, R. Vicente, L. A. López, E. Rubio, M. Tomás, C. Álvarez-Rúa, *J. Am. Chem. Soc.* **2004**, *126*, 470; e) J. Barluenga, R. Vicente, P. Barrio, L. A. López, M. Tomás, *J. Am. Chem. Soc.* **2004**, *126*, 5974; f) J. Barluenga, R. Vicente, L. A. López, M. Tomás, *J. Am. Chem. Soc.* **2006**, *128*, 7050; g) J. Barluenga, R. Vicente, P. Barrio, L. A. López, M. Tomás, J. Borge, *J. Am. Chem. Soc.* **2004**, *126*, 14354; h) J. Barluenga, R. Vicente, L. A. López, M. Tomás, *Tetrahedron* **2005**, *61*, 11327; i) J. Barluenga, R. Vicente, L. A. López, M. Tomás, *J. Organomet. Chem.* **2006**, *691*, 5642.

[19] The double transfer of the carbene and CO ligands in Cr−N−heterocyclic carbenes to platinum complexes is also known, see: M. Berry, M. Gil, J. A. K. Howard, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1980**, 1625.

[20] R. F. W. Bader, *Atoms in Molecules—A Quantum Theory*, Clarendon, Oxford, **1990**.