Further investigations of the diverse reactivity of 2 as well as investigations into the chemistry of other alkene complexes of group 4 metals are ongoing in our laboratory.

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Supplementary Material Available: An experimental section containing details of the preparation and spectroscopic characterization of compounds, a listing of crystallographic data and a description of data collection procedures, an ORTEP diagram of 2, and listings of final positional and thermal parameters, bond distances and angles, torsion angles, and least-squares planes (32 pages); a listing of structure factors (25 pages). Ordering information is given on any current masthead page.

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Alkyl Group Isomerization Studies with Unusually Stable Alkylmetal Complexes of Palladium and Platinum. Secondary-Primary Alkyl Isomerization Equilibria in the Absence of Steric Influences from Ancillary Ligands

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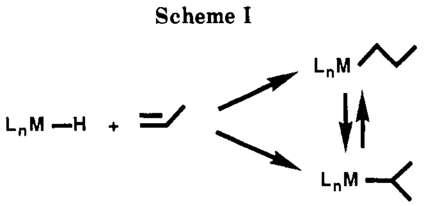
Summary: The unusually stable palladium(II) and platinum(II) derivatives $[R_2NCS_2]M(PR'_3)(alkyl)$ (R = Me, Et; R' = Et, Ph) undergo isomerization of the alkyl ligand when heated (Pt, 120 °C; Pd, 75 °C) in solution. For primary/secondary alkyl pairs (alkyl = *n*-propyl/isopropyl, *n*-butyl/*sec*-butyl) the positions of the isomerization equilibria are similar, 9/1.0 for platinum and 10/1.0 for palladium. This 1.6–1.7 kcal/mol free energy difference between the isomers represents the bond energy difference of primary versus secondary alkylmetal complexes in the absence of steric constraints imposed by other ligands in the coordination sphere.

Scheme I



The insertion of alkenes into metal–hydride bonds, a reaction that is important to many processes catalyzed by transition metals,[1] can lead to isomeric mixtures of alkylmetal complexes (Scheme I). The various isomers, which are generally in rapid equilibrium, can control the types of products produced in these reactions.[2] While a number of alkyl isomerization reactions of alkylmetal complexes have been reported,[3-7] fundamental information on the factors that determine the bonding preferences is still lacking. We report here investigations with unusually stable palladium(II) and platinum(II) derivatives of the formula $[R_2NCS_2]M(PR'_3)(alkyl)$ (R = Me, Et; R' = Et, Ph) in which the isomerization of the alkyl ligand (e.g., isopropyl, *n*-propyl) can be carefully studied by varying the ancillary ligands and the alkyl group. An important feature of the system is the ability to prepare complexes in which the ancillary ligands have minimal steric influences on the alkyl isomerization reaction. Steric effects have dominated earlier studies.

The new $[R_2NCS_2]M(PR'_3)(alkyl)$ complexes are prepared from the reaction of $[R_2NCS_2]M(PR'_3)Cl$ with alkyllithium or Grignard reagents.[8] With platinum, the synthesis is successful for alkyl = methyl for both R' = Et and R' = Ph, but stable alkylpalladium complexes containing β-hydrogen atoms, such as the *n*-propyl and isopropyl complexes, have only been prepared for R' = Et. The complexes $[Me_2NCS_2]Pd(PEt_3)(Pr)$ can be heated in toluene solution at 60 °C for extended periods without noticeable decomposition, and at 75 °C decomposition is ca. 1%/h. These complexes appear to be the most thermally stable simple alkyl derivatives containing β-hydrogen atoms that have been prepared for this metal. In general, palladium complexes with nonchelated alkyl ligands containing β-hydrogen atoms are not stable above room temperature.[9] The platinum complexes can be prepared for

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(8) (a) For $[R_2NCS_2]Pt(PEt_3)(alkyl)$ complexes see: Reger, D. L.; Baxter, J. C.; Garza, D. G. *Organometallics* **1990**, *9*, 16. (b) The $[Me_2NCS_2]Pt(PPh_3)(alkyl)$ and $[Me_2NCS_2]Pd(PEt_3)(alkyl)$ complexes are prepared in a fashion analogous to that for the complexes reported in ref 8a and have been fully characterized by NMR and mass spectroscopy and combustion analysis.

(9) The complexes *cis*- and *trans*-$[Pd(Et)_2(PMe_2Ph)_2]$ decompose in solution at room temperature and are "too unstable for microanalysis".[10] $Pd(DPPE)(Et)_2$ decomposes rapidly in solution at 60 °C.[10b] $CpPd(PPh_3)(Bu)$ decomposes in solution at 35 °C and $CpPd(PPh_3)(CH_2CH_2CH(COMe)_2)$ at 50 °C.[11] The low thermal stability of alkylpalladium complexes with β-hydrogen atoms has been extensively exploited in organic synthesis.[12]

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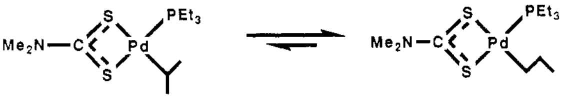
both R′ = Et and R′ = Ph and are also extremely thermally stable. They can be heated at 130 °C for extended periods with no measurable decomposition.

At these elevated temperatures, the alkyl complexes undergo a slow isomerization reaction ($t_{1/2}$ of ca. 8 h at 130 °C for platinum and 5 h at 75 °C for palladium) of the alkyl ligand in aromatic solvents (eqs 1–4). In all cases,


(1)

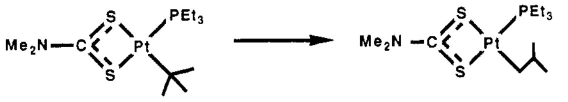

(2)


(3)


(4)

both isomers have been prepared directly and equilibrate to the mixtures shown. The positions of the isomerization equilibria at 120 °C are 9/1.0 (primary/secondary isomer) for all three of the platinum cases.[13] For the palladium reaction it is 10/1.0 at 75 °C. As expected, the isomer with the metal bonded to a primary carbon is favored, but substantial amounts of the secondary isomer are present in the equilibrium mixtures. In the platinum system, substituting PEt_3 with the sterically more demanding PPh_3 ligand or changing the alkyl ligand from propyl to the sterically larger butyl ligand has little effect on the ratio of secondary/primary isomer. This indicates that the equilibria are not greatly influenced by steric contributions from the dithiocarbamate and phosphine ligands. The lack of steric crowding by the ancillary ligands has been verified crystallographically.[14] The 9/1.0 ratio of primary to secondary alkyl isomers for platinum at 120 °C is a free energy difference of 1.7 kcal/mol, while the 10/1.0 ratio for palladium at 75 °C is 1.6 kcal/mol. We believe that this represents the bond energy difference in primary versus secondary alkyls for these metals in the absence of steric constraints imposed by other ligands in the coordination sphere. Other estimations of these differences contain both steric and electronic contributions and are generally at least 5 kcal/mol.[15] For comparison, the energy difference in a C–H bond for primary versus secondary carbon atoms is ca. 3 kcal/mol.[16] The lower value for the transition-metal complexes may simply reflect the longer M–C bond distances, although other factors such as electronegativity differences could also be important.

The *tert*-butyl complex, $[Me_2NCS_2]Pt(PEt_3)(t\text{-}Bu)$, has also been prepared. It is also unusually stable but completely isomerizes to the primary isomer at 120 °C (eq 5).


(5)

Thus, the energy difference for a primary over a tertiary metal–carbon bond must be at least 4 kcal/mol.

Only a limited number of isomerization reactions of this type have been investigated previously. Our observations of substantial amounts of secondary carbon isomers at equilibrium are contrasted by the fact that in the $CpFeCO(PPh_3)(alkyl)$,[3] $IrZI(CO)L_2(alkyl)$ (Z = Cl, I; L = PMe_3, PMe_2Ph),[4d] and $RIrCl_2(CO)(PPh_3)_2$[4a,c] systems the secondary isomers rearrange completely to the primary isomers. In these systems, a significant contribution to the position of the isomerization reaction is expected from the steric effects of the bulky ancillary ligands, an effect clearly favoring the primary isomers. A similar result is observed with *cis*-$Pt(PPh_3)_2Et(alkyl)$ complexes.[5] Although this case is somewhat similar to the system being studied here, the cis phosphines are sterically bulky and will influence the equilibrium position. Only in the dimeric system $[Ir(CO)_2Cl(\mu\text{-}Cl)R]_2$, which was described as having low steric constraints, were substantial amounts of both primary and secondary isomers noted.[4b] Also, *trans*-(t-Bu)Me_2AuPPh_3 isomerizes completely to *trans*-(i-Bu)Me_2AuPPh_3.[6]

The platinum and palladium system outlined here is designed to study the isomerization of an alkyl ligand by systematically varying the metal, the phosphine ligand, and the alkyl ligand itself. We plan to study electronic and steric effects on the stability of the alkylmetal isomers by further varying these groups. This is fundamental information in many catalytic processes, such as the hydroformylation reaction, that involve alkylmetal intermediates.[1]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also partially supported by a grant from the University of South Carolina Venture Fund. The NSF (Grant Nos. CHE-8411172 and CHE-8904942) and NIH (Grant No. RR-02425) have supplied funds to support NMR equipment, and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment.

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Contribution of Olefinic Ring Strain to $(CO)_5Cr$–Cyclooctene Bond Strengths

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Summary: The Cr–olefin bond in $Cr(CO)_5$(cyclooctene) complexes was found to be 5 kcal/mol stronger for *trans*-cyclooctene than for *cis*-cyclooctene. The similarity of the rates of reaction of photochemically generated $Cr(CO)_5S$ with free *cis*- or *trans*-cyclooctene suggests that steric factors contribute little to this difference.

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