ments, in this case the earlier reported propensity of bridging carbene complexes to undergo metal–fragment interchange[1] destroys the molecular integrity necessary for analysis of such experiments. We can therefore write a reasonable mechanism for the migration reaction which accounts for our product and labeling results, but we do not yet know whether the moiety which migrates in the actual reactive species is mono- or dinuclear.

Such a mechanism, illustrated for the observed conversion of **3g** to **3e**-d_4, is shown in Scheme IV. We believe the first step in the process involves migration of metal and a hydrogen atom in opposite directions (perhaps via a β-elimination/reductive elimination sequence), leading to π-complex **5**. Given that one-carbon migration occurs in the closely related rearrangement of **3a**, it may be possible to do the same sort of process in reverse, leading to **6**. However, the labeling results rule out this direct 1,2 metal/H interchange as the *predominant* path in the case of **3g**, because that would lead to the (unobserved) labeling pattern shown in the scheme as resulting directly from **6**. Instead, π-complex **5** apparently more rapidly undergoes insertion into the methyl C–H bond, leading to π-allyl complex **7**. Reductive elimination leads to **8**, and then 1,2 metal/H interchange can occur, leading to the labeling pattern actually found[7] in **3e**.

The π-complexes **5** and **8** are obvious precursors for the pentenes formed as major products in the reaction. However, given the often demonstrated reversibility of π-complex formation between low-valent metals and olefins, if this mechanism is correct, it suggests that free olefin becomes reincorporated into the manifold of intermediates (i.e., there is a viable pathway for conversion of alkenes into dinuclear carbene complexes). If the reentry rate is slow enough, it may be difficult to detect incorporation of olefin in the time required for complete rearrangement of a given internal alkylidene, but we decided to test this prediction. First, we carried out the thermolysis of deuterium-labeled 2-propylidene complex **3f** in the presence of unlabeled propene. Isolation of the terminal alkylidene product **3c** and mass spectral analysis showed that it did, in fact, contain a small but significant amount (ca. 6%) of alkylidene-h_6, without contamination by mixed H/D species which might have arisen by a hydrogen (rather than alkylidene ligand) exchange process. Second, we examined the rearrangement of unlabeled **3c** in the presence of an excess of propene. In this experiment, detectable amounts (ca. 1%) of 1-propylidene complex **3b** appear in place of the 1-pentylidene rearrangement product **3e** formed in the absence of propene.[8]

Whether or not the intermediates in Scheme IV are dinuclear, if stable mononuclear carbene complexes can be prepared with *n*-alkyl chains attached to the alkylidene carbon, it seems likely that carbon-to-carbon migrations analogous to those we have found might occur. In addition, it is perhaps reasonable to point out that the alkylidene/π-complex interconversions illustrated in Scheme IV constitute a mechanism for alkene isomerization. In our particular system it appears that even though this path is accessible, isomerization via π-allyl complexes is more rapid (e.g., **5** is apparently converted to **7** faster than it rearranges to **6**). However, the alkylidene route may in some cases turn out to be the favored pathway. In any case it should certainly now be considered as a viable alternative to the more conventional[9] π-allyl and metal hydride addition/elimination mechanisms.

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Registry No. 1, 62602-00-0; **3a**, 79255-80-4; **3b**, 79255-81-5; **3c**, 79255-82-6; **3d**, 79255-83-7; **3e**, 79255-84-8; **3f**, 79255-85-9; **3g**, 79272-65-4; **4a**, 79255-86-0; **4c**, 79255-87-1; **4d**, 79255-88-2; 2,2-diiodopropane, 630-13-7; 1,1-diiodopropane, 10250-52-9; 3,3-diiodopentane, 66688-39-9; 2,2-diiodopentane, 66688-37-7; 1,1-diiodopentane, 66688-35-5; 1,1,1,3,3,3-hexadeuterio-2,2-diiodopropane, 79255-38-2; 2,2,4,4-tetradeuterio-3,3-diiodopentane, 79255-39-3.

Supplementary Material Available: Spectral and Analytical data on complexes **3a–g 4a**, and **4c** (2 pages). Ordering infor-

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[7] It is also obviously important to examine the labeling pattern in the one-carbon migration product **3d** formed from **3g**. However, the small amounts of this material which build up in the thermolysis of **3g** have so far made isolation of enough material for careful NMR analysis very difficult. We are presently investigating the possibility of carrying out this isolation by preparative HPLC; if this is successful, we should be able to test the prediction that the one-carbon migration gives a labeling pattern corresponding to that illustrated in **6** (Scheme IV).

[8] A reviewer has asked whether there is any possibility that the **3b** formed during the rearrangement of **3c** in the presence of propene might be due to the occurrence of some olefin metathesis under the reaction conditions. We feel this interesting possibility is unlikely, since we are unable to detect either metathesized olefins or other alkylidenes (e.g., we see neither the parent complex **3**, R = R′ = H, nor the ethylidene complex **3**, R = H, R′ = Me) during this process.

[9] (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980; pp 33–35. See also, for example: (b) Casey, C. P.; Cyr, C. R. *J. Am. Chem. Soc.* **1973**, *95*, 5811. (d) Green, M.; Hughes, R. P. *J. Chem. Soc., Commun.* **1975**, 619.

Free Radical Reactions of $HCo(CO)_4$

Theodore E. Nalesnik and Milton Orchin*

Department of Chemistry, University of Cincinnati
Cincinnati, Ohio 45221

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Summary: A CIDNP effect has been observed when 1,1-diphenylethylene is reacted at low temperature with $HCo(CO)_4$. This and other chemical evidence clearly demonstrate radical formation.

It has been suggested that the reaction of $HCo(CO)_4$ with 1,1-diphenylethylene[1a] (and related compounds[1b]) proceeds by a radical mechanism (Scheme I), but no evidence for the presence of radicals could be secured. We have restudied this reaction and wish to report the first example of a CIDNP effect observed with $HCo(CO)_4$.

When 1,1-diphenylethylene is injected into a NMR tube containing a CH_2Cl_2 solution of $HCo(CO)_4$ at −78 °C and the tube placed immediately in a ^1H NMR cavity at 31 °C, the CIDNP effect shown in Figure 1 is observed. The proton signal of the methyl group in the product at δ 1.6 shows a doublet emission which quickly changes to a doublet absorption with an upfield shift as the reaction proceeds with the rise in temperature.

The CIDNP effect represents evidence for the intermediacy of the geminate radical pair $\overline{Ph_2\dot{C}CH_3\dot{C}o(CO)_4}$ formed by diphenylethylene abstracting hydrogen from $HCo(CO)_4$ (Scheme I). If it is assumed that the geminate radical pair is derived from a singlet precursor and that the *g* factor for $\dot{C}o(CO)_4$ (2.137 ± 0.01)[2] is larger than that for $Ph_2\dot{C}CH_3$, with a positive coupling constant, *a*, for a $\dot{C}$–CH type radical, application of the Kaptein formulation[3] predicts the observed emission spectrum.

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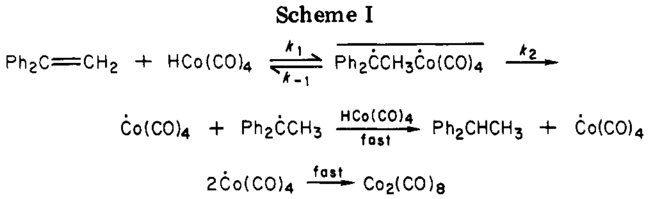
[1] (a) J. A. Roth and M. Orchin, *J. Organomet. Chem.*, **182**, 299 (1979); (b) T. E. Nalesnik and M. Orchin *ibid.*, **199**, 265 (1980).

[2] R. L. Sweany, *Inorg. Chem.*, **19**, 3512 (1980).

[3] R. Kaptein, *J. Chem. Soc. D.*, 732 (1971). T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976, p 537.

Scheme I



It has been reported that when Ph_2CHBr is reacted with $Co_2(CO)_8$ in THF, $Ph_2CHCHPh_2$ is formed in good yield.[4] The THF disproportionates $Co_2(CO)_8$ to provide $[Co(CO)_4]^-$, and this anion reacts with the bromide to give $Ph_2\dot{C}H$ as an intermediate which couples to the observed dimer. When we repeated this experiment in the presence of $HCo(CO)_4$, Ph_2CH_2 was obtained in 95% yield. Apparently the radical intermediate abstracts hydrogen from $HCo(CO)_4$ faster than it dimerizes. Ph_2CHBr in THF reacts with $HCo(CO)_4$ in the absence of added $Co_2(CO)_8$ to give Ph_2CH_2, but the reaction is probably initiated by $[Co(CO)_4]^-$ available either from the strongly acidic[5] $HCo(CO)_4$ or from the disproportionation of $Co_2(CO)_8$ generated from the decomposition of $HCo(CO)_4$ in THF.[6]

The hydrogenation of α-methylstyrene with $HMn(CO)_5$, after which Scheme I is modeled, has also been reported to show a CIDNP effect.[7] The reported second-order rate law, inverse isotope effect, and deuterium exchange between reactants and products for $HMn(CO)_5$ reactions with α-methylstyrene are also characteristic of our reactions with $HCo(CO)_4$,[1] suggesting similar mechanisms for hydrogenations with $HMn(CO)_5$ and $HCo(CO)_4$.

$HCo(CO)_4$ was prepared as previously described.[1b] **$Ph_2C{=}CH_2$** was purchased from the Aldrich Chemical Co. **CIDNP** effects were observed on a Varian T 60-MHz ^1H NMR spectrophotometer.

CIDNP Effect with 1,1-Diphenylethylene. A 500-μL aliquot of freshly prepared 0.80 M (0.40 mmol) $HCo(CO)_4$ was injected into a NMR tube capped with a rubber septum and flushed well with CO. The NMR tube was then placed in a CO_2/acetone bath at −78 °C. The tube was then removed from the bath, and 40 μL (0.22 mmol) of 1,1-diphenylethylene was quickly injected into the $HCo(CO)_4$ solution. The NMR tube was then shaken vigorously for 2 s, wiped clean, and immediately placed in the NMR cavity at 31 °C. The spectrum is quickly scanned in the methyl proton region in order to observe the transient emission spectrum. The elapsed time between the injection of the olefin and the beginning of the spectrum scan must be 15–25 s or only an absorption spectrum will be observed. The entire reaction is over in about 60 s.

Reaction of $HCo(CO)_4/Co(CO)_4^-$ with Bromodiphenylmethane. In a 200-ml round-bottom flask well flushed with CO was placed a 78-mL THF solution of 0.185 M (14.0 mmol) $HCo(CO)_4$. To the solution was added 2.4 g (4.9 mmol) of $Co_2(CO)_8$ followed by the addition of 1.2 g (4.9 mmol) of bromodiphenylmethane dissolved in 5 mL of THF. The solution was stirred for 12 h at room temperature. The solvent was then evaporated and the residue redissolved in 70 mL of CH_2Cl_2. To this solution was then added dropwise 5 mL of ethylenediamine. The solution was then washed with H_2O, 2% aqueous HCl, and saturated aqueous NaCl before drying over $CaCl_2$ and filtering. Evaporation of the solvent gave a clear oil, 0.78 g (95% yield). Analysis by ^1H NMR showed it to be essentially pure diphenylmethane. ^1H NMR ($CDCl_3$): δ 7.1 (s, 10, phenyls), 3.9 (s, 2, methylene). When the above reaction was repeated in the absence of added $Co_2(CO)_8$, an 80% yield of Ph_2CH_2 was obtained; no coupled product could be detected (^1H NMR).

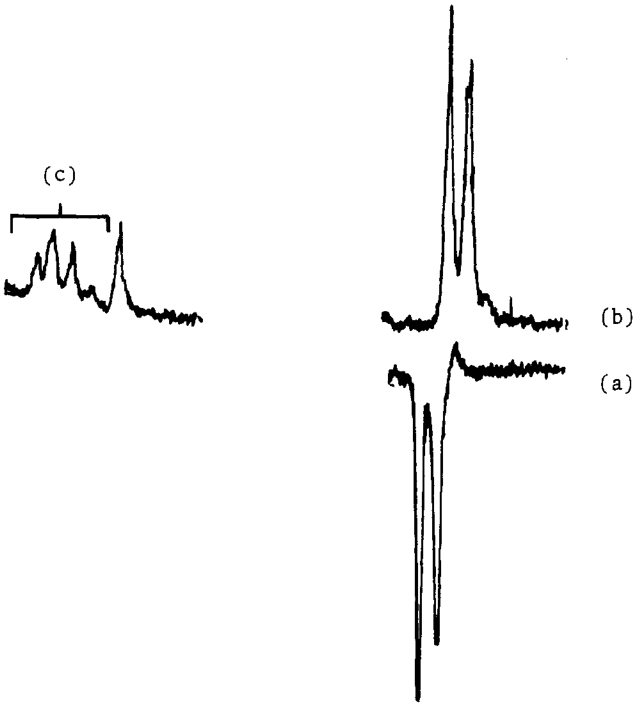


Figure 1. ^1H NMR spectra: (a) emission spectrum of Ph_2CHCH_3; (b) absorption spectrum of Ph_2CHCH_3 observed 20 s after a; (c) spectrum of Ph_2CHCH_3 with spinning side band of CH_2Cl_2.

Registry No. $HCo(CO)_4$, 16842-03-8; $Co_2(CO)_8$, 10210-68-1; 1,1-diphenylethylene, 530-48-3; bromodiphenylmethane, 776-74-9.

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(5) T. E. Nalesnik and M. Orchin, *J. Organomet. Chem.*, **212**, C16 (1981).

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(7) R. L. Sweany and J. Halpern, *J. Am. Chem. Soc.*, **99**, 8335 (1977).

Intermetallic Chalcogenide Atom Transfer and the Synthesis of 1,4-$[(CH_3C_5H_4)_2Ti]_2S_4$

C. Mark Bolinger, John E. Hoots, and Thomas B. Rauchfuss*

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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Summary: $(C_5H_4R)_2TiE_5$ (R = H, CH_3; E = S, Se) efficiently transfer a dichalcogenide fragment to $[Ir(Ph_2PCH_2CH_2PPh_2)_2]Cl$ affording $Ir^{III}E_2$ complexes and in one case 1,4-$[(C_5H_4CH_3)_2Ti]_2S_4$. The unique Ti_2S_4 heterocycle can also be prepared via the PBu_3 desulfurization of $(C_5H_4CH_3)_2TiS_5$.

This report describes a new intermetallic atom transfer reaction[1] and the synthesis of a very unusual organotransition metal chalcogenide. The key reagents employed in this study are the dicyclopentadienyltitanium(IV) pentachalcogenides whose structures are composed of metallapentachalogenide rings.[2] The reactivity of these

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(1) For other examples of intermetallic atom transfer reactions see: Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248–1253. Reynolds, J. G.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 1873–1878.

(2) Epstein, E. F.; Bernal, I. *J. Organomet. Chem.* **1971**, *26*, 229–245. Muller, K. G.; Petersen, J. L.; Dahl, L. F. *Ibid.* **1976**, *111*, 91–112.

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