[3] For a recent comprehensive review of lattice interpenetration see: S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.

[4] Crystal data for **1**: $C_{18}H_{12}N_{14}O_2Zn.6C_3H_7NO$, $M_r = 960.36$, clear octahedron, $0.30 \times 0.23 \times 0.20$ mm, orthorhombic, space group *Fddd*, $a = 16.638(5)$, $b = 20.198(3)$, $c = 26.273(3)$ Å^3, $V = 8829(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.445$ g cm^{-3}, $\mu(Cu_{K\alpha}) = 1.400$ mm^{-1}, $F(000) = 4032$. Siemens P4 diffractometer, graphite-monochromated $Cu_{K\alpha}$ radiation, ω scans, $T = 293$ K. Of 1650 independent reflections measured ($2\theta < 120°$), 1156 had $I_o > 2\sigma(I_o)$ and were considered observed. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$ and allowed to ride on their parent carbon atoms. Refinement was by full-matrix least-squares based on F^2 to give $R_1 = 0.0767$, and $wR_2 = 0.2143$. Computations were carried out with the SHELXTL 5.03 program package. The included DMF solvent was distributed randomly throughout the channels in the structure and no realistic atom positions could be fitted to the weak diffuse areas of residual electron density. The value of about six DMF molecules per zinc atom given in the empirical formula was deduced from the TGA measurements and the corresponding values of calculated density, μ, and $F(000)$ reflect this figure. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102315. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[5] A search of the April 1998 release of the Cambridge Crystallographic Database revealed only three other examples of a linear M-O-C arrangement out of a total of 1787 hits.

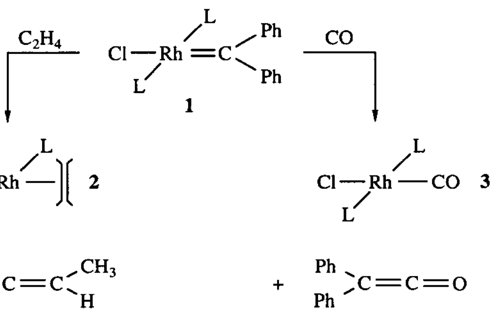
[6] A substantial portion of the powder pattern of the heated sample comprises an amorphous "hump" but with the principal lines of the host structure clearly visible.

The First Example of Linkage-Isomeric Ketene Metal Complexes[**]

Elke Bleuel, Matthias Laubender,
Birgit Weberndörfer, and Helmut Werner*

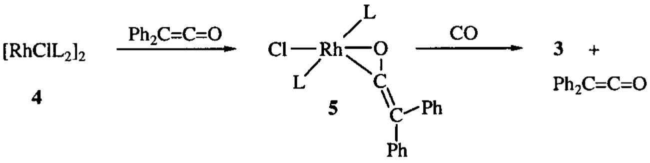
*Dedicated to Professor Otto J. Scherer
on the occasion of his 65th birthday*

In the course of investigations on the reactivity of carbenerhodium complexes *trans*-$[RhCl(=CR'_2)(L)_2]$ ($R' =$ aryl; $L = PR_3$, AsR_3, SbR_3) we recently observed[1] that these compounds react smoothly with olefins, CO, and isocyanides by C–C coupling. While the reaction of **1** with ethene affords besides **2** exclusively 1.1-diphenylpropene (and *not* 1.1-diphenylcyclopropane), treatment of **1** with CO forms the carbonyl complex **3** and diphenylketene (Scheme 1).[1, 2]



Scheme 1. $L = PiPr_3$.

Since it is known from the work by the groups of Herrmann, Cutler, Roper, and others that reactions of both metal carbonyls with diazoalkanes and of metal carbenes with CO under pressure lead to ketene complexes,[3] we were interested to find out whether the metal-assisted formation of $Ph_2C{=}C{=}O$ from **1** and CO occurs via the intermediate *trans*-$[RhCl(Ph_2C{=}C{=}O)(PiPr_3)_2]$. Attempts to detect such a compound by controlled addition of CO to a solution of **1** in C_6D_6 or $CDCl_3$ failed. Therefore we chose a different synthetic route for our target, the square-planar ketenerhodium complex, and treated the chloro-bridged binuclear compound **4**[4] with diphenylketene. In benzene at room temperature complex **5** (Scheme 2) is readily formed and, after removal of the solvent, is isolated as a red-brown solid in almost quantitative yield. The coordination of diphenylketene through the C=O and not the C=C bond, which was already indicated by the spectroscopic data,[3c] was confirmed by an X-ray crystal structure analysis (Figure 1).[5] The coordination geometry around the rhodium atom is distorted square-planar, the bond angle P1-Rh-P2 of 168.41(4)° thereby deviates considerably from the ideal value of 180°. We assume that this is due to the repulsion between the isopropyl and phenyl groups. Moreover, a remarkable feature is that in contrast to Cl-Rh-C1 (146.32(1)°) the axis Cl-Rh-O (177.25(9)°) is nearly linear and thus unsymmetrical bonding of the C=O unit to the metal center results. Compared to other $\eta^2(C,O)$-diphenylketene complexes,[6] the distance O–C1 in **5** is significantly shorter which points to a reduced degree of π-back bonding from the rhodium center to the π* orbital of the C=O moiety. In view of the presence of the electron-rich $[RhCl(PiPr_3)_2]$ fragment this observation is really surprising.



Scheme 2. $L = PiPr_3$.

The ketene complex **5**, which is thermally remarkably stable, reacts with CO under normal pressure to yield quantitatively the rhodium carbonyl compound *trans*-$[RhCl(CO)(PiPr_3)_2]$[7] and diphenylketene. Upon treatment of **5** with C_9H_7K in THF a substitution of chloride for indenyl does not occur. However, the desired ligand exchange can be carried out if compound **5** is transformed in the initial step with one equivalent of $AgPF_6$ to an intermediate with the supposed composition *trans*-$[Rh(Ph_2C{=}C{=}O)(PiPr_3)_2(O{=}CMe_2)]PF_6$, which subsequently reacts in situ with

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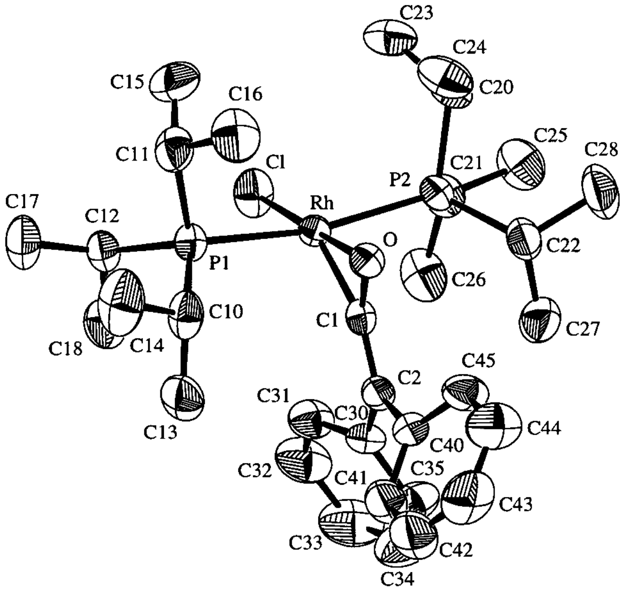
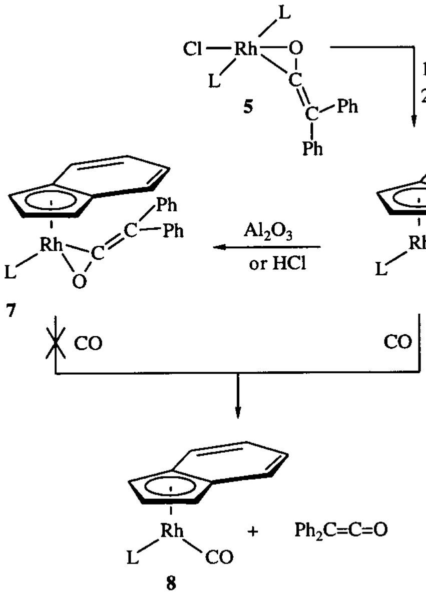


Figure 1. Molecular structure of **5** (thermal elipsoids with 50% probability). Selected bond lengths [Å] and angles [°]: Rh–O 2.090(3), Rh–C1 1.971(4), Rh–Cl 2.298(1), Rh–P1 2.382(1), Rh–P2 2.369(1), C1–O 1.264(5), C1–C2 1.349(6); P1-Rh-P2 168.41(4), Cl-Rh-O 177.25(9), Cl-Rh-C1 146.32(1), P1-Rh-Cl 90.02(4), P2-Rh-Cl 90.28(4), P1-Rh-O 88.37(8), P2-Rh-O 90.85(8), Rh-O-C1 66.8(2), Rh-C1-C2 144.0(3), O-C1-C2 138.9(4).



Scheme 3. L = P*i*Pr$_3$.

C_9H_7K to give the indenyl complex **6** (Scheme 3). By using this method, **6** can be isolated in 86% yield. Spectroscopic data reveal that the conversion of **5** to **6** is accompanied by a change of the coordination mode of the ketene ligand from $\eta^2(C,O)$ to $\eta^2(C,C)$. The IR spectrum of **6** displays an absorption at 1777 cm^{-1} for the C=O stretch (**5**: $\tilde{\nu}$(C=O) = 1590 cm^{-1}) and the ^{13}C NMR spectrum a doublet of doublets at $\delta = 227.7$ for the C=*C*=O and a doublet at $\delta = 19.5$ for the *C*=C=O carbon atom (**5**: $\delta = 167.4$ (dt) and 123.9 (s)). The X-ray crystal stucture analysis of **6** confirms the proposed linkage isomerization of the metal-bound ketene (Figure 2).

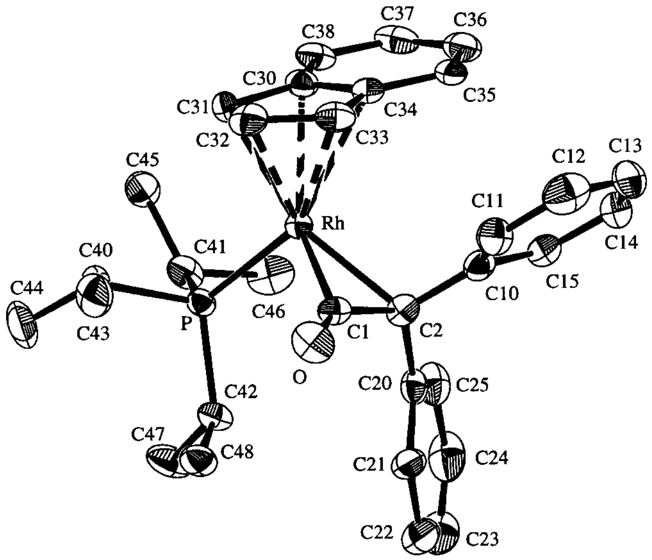
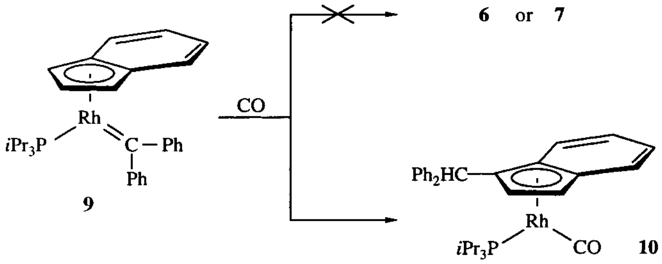


Figure 2. Molecular structure of **6** (thermal elipsoids with 50% probability). Selected bond lengths [Å] and angles [°]: Rh–C1 1.936(5), Rh–C2 2.180(5), Rh–P 2.321(1), Rh–C30 2.461(5), Rh–C31 2.263(5), Rh–C32 2.242(4), Rh–C33 2.271(5), Rh–C34 2.451(5), O–C1 1.208(4), C1–C2 1.467(5); P-Rh-C1 98.1(2), P-Rh-C2 103.9(1), Rh-C1-O 139.6(4), Rh-C2-C1 60.4(2), C1-Rh-C2 41.2(2), O-C1-C2 142.0(5).

The C1–C2 bond is longer and the C1–O bond shorter than in **5**. The difference of the Rh–C1 bond length in **5** and **6** is quite small and also the bond angle O-C1-C2 is almost identical in both complexes. The indenyl ligand in **6** is unsymmetrically linked (i.e. approaching η^3 coordination) to the metal, as was also found in other rhodium complexes of the general composition [(C_9H_7)RhL_2] and [(C_9H_7)RhL(L′)].[8]

Although compound **6** is thermally stable up to 137°C, upon treatment with acidic Al_2O_3 or with a solution of HCl in benzene it rapidly rearranges to the isomeric complex **7**. The isomerization, which can be monitored by the change of color from orange-red to orange, is confirmed by the spectroscopic data. Characteristic features for **7** are the position of the $\tilde{\nu}$(C=O) stretching frequency at 1598 cm^{-1} (see for comparison the data for **5** and **6**) and the chemical shift of the signals for the carbon atoms of the C=C=O unit at $\delta = 223.0$ and 130.2. With regard to the reactivity, compounds **6** and **7** differ insofar as the $\eta^2(C,C)$-bonded isomer reacts instantaneously with CO to yield the carbonylrhodium complex **8** (plus diphenylketene), while the $\eta^2(C,O)$-bonded isomer is completely inert toward carbon monoxide (C_6H_6, 25°C, 1 bar, 5 days).

The attempt to generate either compound **6** or **7** by metal-assisted C–C coupling from the carbene complex **9** (recently prepared in our laboratory)[8d] and CO led to a surprising result. Instead of a coupling of the CPh_2 moiety with CO, after attack of CO at the metal center a migration of the carbene to the indenyl ligand takes place, which is accompanied by an insertion of CPh_2 into one of the C–H bonds of the five-membered ring of C_9H_7. The structure of **10** (Scheme 4) has been confirmed by X-ray crystallography.[9] Complex **9** thus behaves differently to the corresponding cyclopentadienyl



Scheme 4.

analogue [(η^5-C$_5$H$_5$)Rh(=CPh$_2$)(P*i*Pr$_3$)] which reacts with CO to give [(η^5-C$_5$H$_5$)Rh(CO)(P*i*Pr$_3$)] and diphenylketene.[1b]

With the synthesis and the characterization of compounds **6** and **7** we have shown for the first time that linkage isomerism exists also among ketene transition metal complexes. Up to now examples for this type of isomerism were known mainly for metal compounds containing NO$_2^-$, NCS$^-$, and triazole derivatives as ligands,[10] the stability of the respective isomers could usually be predicted by the hard/soft acid/base (HSAB) concept.[11] Since only a conversion of **6** to **7** but not in the reverse direction takes place, we assume that the η^2(*C*,*O*)-bonded isomer is thermodynamically more stable. We are now attempting to prepare rhodium and iridium complexes with different configurations as well as oxidation states of the metal using not only Ph$_2$C=C=O but also other ketenes as ligands in an effort to establish under which circumstances the η^2(*C*,*O*)- or the η^2(*C*,*C*)-coordination mode of a particular ketene is preferred.

Experimental Section

5: A solution of **4** (238 mg, 0.26 mmol) in benzene (5 mL) was treated with diphenylketene (88 µL, 0.52 mmol) and stirred for 5 min at room temperature. The solvent was removed in vacuo, the red-brown solid was washed twice with pentane (10 mL) and dried; yield 296 mg (87 %); m.p. 110 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$(C=C=O) = 1590 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$):[12] δ = 8.76, 7.66, 7.39–6.98 (all m, C$_6$H$_5$), 2.33 (m, PC*H*CH$_3$), 1.19 (dvt, *N* = 13.5, ^3J(H,H) = 6.8 Hz, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (50.3 MHz, C$_6$D$_6$): δ = 167.4 (dt, ^1J(Rh,C) = 19.5, ^2J(P,C) = 4.9 Hz, C=*C*=O), 138.4, 137.6, 130.2, 129.4, 129.1, 128.9, 128.7, 128.3, 127.8, 127.6 (all s, C$_6$H$_5$), 123.9 (s, *C*=C=O), 22.2 (vt, *N* = 19.5 Hz, P*C*HCH$_3$), 19.6, 19.3 (both s, PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$): δ = 32.5 (d, ^1J(Rh,P) = 108.3 Hz).

6: A solution of **5** (117 mg, 0.18 mmol) in acetone (10 mL) was treated dropwise with a solution of AgPF$_6$ (45 mg, 0.18 mmol) in acetone (10 mL). A change of color from red-brown to orange occurred and a white flocky precipitate of AgCl was formed. After the reaction mixture had been stirred for 5 min at room temperature, the solution was filtered. The filtrate was dried in vacuo and the residue was dissolved in THF (10 mL). The solution was treated with C$_9$H$_7$K (139 mg, 0.90 mmol) and stirred for 30 min. After the solvent had been removed, the residue was extracted with pentane (50 mL). The extract was filtered, the filtrate was concentrated to about 10 mL and then stored for 12 h at 0 °C. Orange-red crystals were formed which were washed with small quantities of pentane and dried in vacuo; yield 89 mg (86 %); m.p. 137 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$(C=C=O) = 1777 cm^{-1}; ^{1}H NMR (200 MHz, C$_6$D$_6$):[13] δ = 7.59, 7.12–6.75 (both m, C$_6$H$_5$ and H$^{4\text{-}7}$ of indenyl), 6.07 (dt, ^2J(Rh,H) = ^3J(H,H) = 2.8 Hz, H^2 of indenyl), 4.58 (m, H^{1,3} of indenyl), 1.23 (sept (br), ^3J(H,H) = 7.2 Hz, PC*H*CH$_3$), 0.85 (dd, ^3J(P,H) = 13.4, ^3J(H,H) = 7.2 Hz, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): δ = 227.7 (dd, ^1J(Rh,C) = 22.9, ^2J(P,C) = 5.1 Hz, C=*C*=O), 142.3, 140.3, 133.1, 128.4, 128.3, 128.1, 128.0, 127.2, 126.0, 125.4, 124.9, 123.8 (all s, C$_6$H$_5$), 122.3, 122.2, 119.9, 119.0 (all s, C$^{4-7}$ of indenyl), 115.8 (s, C^{8,9} of indenyl), 99.4 (d, ^1J(Rh,C) = 6.4 Hz, C^2 of indenyl), 68.5 (s (br), C^1, C^3 of indenyl), 27.1 (d, ^1J(P,C) = 19.1 Hz, P*C*HCH$_3$), 20.2 (s, PCH*C*H$_3$), 19.5 (d, ^1J(Rh,C) = 3.8 Hz, *C*=C=O); ^{31}P NMR (81.0 MHz, C$_6$D$_6$): δ = 52.8 (d, ^1J(Rh,P) = 197.1 Hz).

7: A solution of **6** (74 mg, 0.13 mmol) in benzene (5 mL) was treated with a 0.36 M solution of HCl (833 µL, 0.30 mmol) in benzene and stirred for 5 min at room temperature. The solvent was removed in vacuo, the residue was dissolved in pentane (5 mL), and the solution stored for 24 h at 0 °C. Orange crystals were formed which were washed with small quantities of pentane and dried in vacuo; yield 69 mg (93 %); m.p. 122 °C (decomp); IR (C$_6$H$_6$): $\tilde{\nu}$(C=C=O) = 1598 cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.89, 7.45–6.66 (both m, C$_6$H$_5$ and H$^{4\text{-}7}$ of indenyl), 5.85 (m, H^2 of indenyl), 5.28, 5.00 (both m, H^{1,3} of indenyl), 2.23 (m, PC*H*CH$_3$), 0.86 (dd, ^3J(P,H) = 13.1, ^3J(H,H) = 7.2 Hz, PCHC*H*$_3$), 0.82 (dd, ^3J(P,H) = 14.4, ^3J(H,H) = 7.3 Hz, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): δ = 223.0 (dd, ^1J(Rh,C) = 32.6, ^2J(P,C) = 7.1 Hz, C=*C*=O), 141.1, 140.5 (both s, C$_6$H$_5$), 130.2 (s, *C*=C=O), 129.4, 129.2, 129.0, 128.3 (all s, C$_6$H$_5$), 128.2 (s, C^{8,9} of indenyl), 127.6, 127.4, 126.7, 126.6 (all s, C$_6$H$_5$), 123.2, 120.5 (both s, C^{4,7} of indenyl), 104.7 (d, ^3J(Rh,C) = 5.7 Hz, C^5 or C^6 of indenyl), 82.0 (m, C^2 of indenyl), 77.4 (s, C^5 or C^6 of indenyl), 62.9 (d, ^1J(Rh,C) = 9.5 Hz, C^{1,3} of indenyl), 25.0 (d, ^2J(P,C) = 19.1 Hz, P*C*HCH$_3$), 19.6, 19.1 (both s, PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 49.8 (d, ^1J(Rh,P) = 162.8 Hz).

10: A slow stream of CO was passed through a solution of **9** (98 mg, 0.18 mmol) in pentane (10 mL) for 30 s at −78 °C. Upon warming the mixture to room temperature, the color of the deep green solution brightened. The solution was stirred for 30 min, the solvent was removed, and the residue was dissolved in pentane (3 mL), which was saturated with CO. After the solution had been stored for 3 d at −18 °C, an orange-yellow solid precipitated which was washed with small quantities of pentane (−10 °C) and dried in vacuo; yield 81 mg (79 %); m.p. 56 °C; IR (C$_6$H$_{14}$): $\tilde{\nu}$(CO) = 1944 cm^{-1}; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 7.69, 7.24–6.89 (both m, C$_6$H$_5$ and H$^{4-7}$ of indenyl), 6.06 (d, ^3J(Rh,H) = 3.2 Hz, C*H*Ph$_2$), 5.83 (m, H^2 of indenyl), 4.82 (d, ^2J(Rh,H) = 3.2 Hz, H^3 of indenyl), 1.72 (sept (br), ^3J(H,H) = 7.2 Hz, PC*H*CH$_3$), 0.84 (dd, ^3J(P,H) = 14.4, ^3J(H,H) = 7.2 Hz, PCHC*H*$_3$), 0.81 (dd, ^3J(P,H) = 14.0, ^3J(H,H) = 7.2 Hz, PCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C$_6$D$_6$): δ = 196.0 (dd, ^1J(Rh,C) = 89.0, ^2J(P,C) = 21.6 Hz, Rh–CO), 144.3, 144.0, 130.4, 128.9, 128.5, 128.1, 126.5, 126.4 (all s, C$_6$H$_5$), 122.9, 121.2 (both s, C^{4,7} of indenyl), 119.3 (s, C^8 or C^9 of indenyl), 118.6 (s, C^5 or C^6 of indenyl), 117.6 (s, C^8 or C^9 of indenyl), 117.3 (s, C^5 or C^6 of indenyl), 98.5 (dd, ^2J(Rh,C) = 5.2, ^3J(P,C) = 1.7 Hz, *C*HPh$_2$), 97.3 (dd, ^1J(Rh,C) = 13.0, ^2J(P,C) = 3.8 Hz, C^1 of indenyl), 72.3 (d, ^1J(Rh,C) = 3.3 Hz, C^2 of indenyl), 51.0 (d, ^1J(Rh,C) = 1.5 Hz, C^3 of indenyl), 28.0 (d, ^1J(P,C) = 21.2 Hz, P*C*HCH$_3$), 19.8, 19.7 (both s, PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C$_6$D$_6$): δ = 74.3 (d, ^1J(Rh,P) = 194.7 Hz).

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[5] Data for the X-ray structure analyses: **5**: Crystals from pentane at 0 °C, C$_{32}$H$_{52}$ClOP$_2$Rh (653.04); crystal size 0.2 × 0.15 × 0.1 mm; triclinic, space group $P\bar{1}$ (no. 2), $a = 8.7233(4)$, $b = 11.0994(8)$, $c = 18.725(1)$ Å, $\alpha = 93.249(5)$, $\beta = 103.280(5)$, $\gamma = 107.901(6)^\circ$, $Z = 2$, $V = 1663.2(2)$ Å^3, $\rho_{\mathrm{calcd}} = 1.304$ g cm^{-3}; $T = 293(2)$ K; $2\Theta = 48^\circ$; 5595 reflections measured, 5207 were unique ($R_{\mathrm{int}} = 0.0227$) and 4037 observed ($I > 2\sigma(I)$); Enraf-Nonius CAD4 diffractometer, Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated, zirconium filter (factor 15.4); Lp and

empirical absorption corrections (Ψ scan, min. transmission 94.56%). The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0398$, $wR_2 = 0.0729$ (for 4037 reflections with $I > 2\sigma(I)$), $R_1 = 0.0626$, $wR_2 = 0.0859$ (for all 5207 data); data-to-parameter ratio 15.04; residual electron density $+0.349/-0.343$ e Å^{-3}. **6**: crystals from pentane at 0 °C, $C_{32}H_{38}OPRh$ (572.50); crystal size $0.4 \times 0.3 \times 0.2$ mm; monoclinic, space group $P2_1/c$ (no. 14), $a = 9.753(3)$, $b = 13.384(4)$, $c = 20.914(6)$ Å, $\beta = 95.998(14)^\circ$, $Z = 4$, $V = 2714.9(14)$ Å^3, $\rho_{\text{calcd.}} = 1.401$ g cm^{-3}; $T = 173(2)$ K; $2\Theta = 50^\circ$; 3569 reflections measured, 3473 were unique ($R_{\text{int}} = 0.0328$) and 2619 observed ($I > 2\sigma(I)$); Enraf-Nonius CAD4 diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated, zirconium filter (factor 16.4); Lp and empirical absorption corrections (Ψ scan, min. transmission 96.85%). The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0348$, $wR_2 = 0.0604$ (for 2619 reflections with $I > 2\sigma(I)$), $R_1 = 0.0602$, $wR_2 = 0.0683$ (for all 3473 data); data-to-parameter ratio 10.24; residual electron density $+0.239/-0.240$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102818 (**5**) and CCDC-102919 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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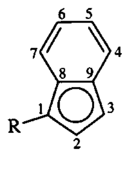
[12] Abbreviations used: vt = virtual triplet, dvt = doublet of virtual triplets, $N = {}^3J(\text{P,H}) + {}^5J(\text{P,H})$ or ${}^1J(\text{P,C}) + {}^3J(\text{P,C})$.

[13] For the numbering of the indenyl carbon (and corresponding hydrogen) atoms see formula **A**.



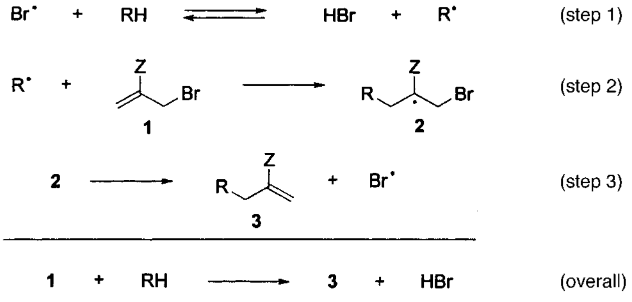
A

Functionalization of Hydrocarbons by a New Free Radical Based Condensation Reaction**

James. M. Tanko* and Mitra Sadeghipour

There is increased awareness of the need to develop new chemical reactions and processes which avoid the use or generation of toxic and/or environmentally threatening materials. Herein we report a newly developed reaction in which a C–H bond of a hydrocarbon is converted into a C–C bond by transfer of an allyl group (R–H → R–C–C=C). This process is especially attractive because (unlike other procedures which effect this conversion) the transformation is accomplished in a single step and does not require strongly acidic or basic reaction conditions, or the use of heavy metals.

The proposed mechanism of this reaction is depicted in Scheme 1. Abstraction of hydrogen from R–H (by Br$^\bullet$) yields R$^\bullet$, which subsequently adds to the C=C bond of a substituted allyl bromide (**1**). Adduct radical **2** undergoes β cleavage to yield product **3** and regenerate Br$^\bullet$. Each step depicted in Scheme 1 is well documented in the literature: A bromine atom exhibits high selectivity in hydrogen atom abstractions (step 1),[1] and is especially reactive towards benzylic hydrogen atoms (for example in the Ziegler bromination).[2] Allyl bromides have been shown to be effective chain transfer reagents in free radical polymerizations, essentially by steps identical to 2 and 3.[3]



Scheme 1. Mechanism of the proposed allyl transfer reaction.

To test whether this chemistry could be coupled as shown in Scheme 1 to "invent" a viable synthetic process, we examined the reaction of several allyl bromides with toluene and cumene (Table 1). Overall, mass balances for these reactions were high, and good to excellent yields were obtained, especially when the allyl bromide possesses a radical-stabilizing substituent (e.g., Z = Ph, CO_2Et, or CN). To confirm the role of Br$^\bullet$ as the chain carrier in this reaction, a series of competition experiments were performed pitting $PhCH_3$

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