ORGANOMETALLICS

.eta.2-(C,O) Ketene coordination at nickel(O). Synthesis, bonding, and molecular structure of (dtbpm)Ni[.eta.2-(C,O)-Ph2C2O] [dtbpm = bis(di-tert-butylphosphino)methane]

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Organometallics, **1992**, 11 (3), 1167-1176• DOI: 10.1021/om00039a024 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

of cold diethyl ether and dried under vacuum at −30 °C: yield 690 mg (87%). Anal. Calcd for $C_{16}H_{34}P_2Pd$ (394.8): C, 48.68; H, 8.68; P, 15.69; Pd, 26.95. Found: C, 48.38; H, 8.70; P, 15.61; Pd, 27.18. IR (KBr, −30 °C): 3125, 3085 cm^{-1} (≡C—H bound), 1619 cm^{-1} (C≡C bound). ^1H NMR (200 MHz, −30 °C): δ 6.91 (m, 2 H, C_2H_2); δ 2.02 ("octet", 4 H, PCH), 1.67 (m, 4 H, PCH_2), 1.11, 1.01 (each m, 12 H, CH_3; phosphane). ^{31}P NMR (−30 °C): δ 69.5.

(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd(C$_2$D$_2$) (11a): synthesis as for **11** but with C_2D_2.

(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd(C$_2$H$_2$) (12). When a suspension of **4** (1.014 g, 2.00 mmol) in diethyl ether (20 mL), containing dissolved ethyne (100 mL) in excess, is warmed from −30 to 0 °C, cooled to −30 °C, and cooled further to −78 °C, colorless crystals form. After the supernatant liquid is removed through a capillary, the crystals are washed with cold ether and dried under vacuum at −30 °C; yield 810 mg (90%). Anal. Calcd for $C_{20}H_{42}P_2Pd$ (450.9): C, 53.28; H, 9.39; P, 13.74; Pd, 23.60. Found: C, 52.88; H, 9.67; P, 13.61; Pd, 23.78. IR (KBr): 3125 cm^{-1} (≡C—H bound), 1626 cm^{-1} (C≡C bound). ^1H NMR (400 MHz, 27 °C): δ 6.78 (m, 2 H, C_2H_2); δ 1.80 (m, 4 H, PCH_2), 1.23 (m, 36 H, CH_3; phosphane). ^{13}C NMR (75.5 MHz, −30 °C): δ 105.1 (m, 2 C, ^1J(CH) = 211 Hz, C_2H_2); δ 34.3 ("t", 4 C, $PCMe_3$), 30.6 (m, 12 C, CH_3), 24.5 (m, 2 C, PCH_2; phosphane). ^{31}P NMR (27 °C): δ 91.3.

(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd(C$_2$D$_2$) (12a): synthesis as for **12** but with C_2D_2. IR (KBr): 2418 cm^{-1} (≡C—D bound), 1531 cm^{-1} (C≡C bound).

{(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd}$_2$(μ-C$_2$H$_2$) (13). A solution of the ethyne complex **11** (790 mg, 2.00 mmol) in diethyl ether (20 mL) is added at −50 °C to solid **1** (902 mg, 2.00 mmol). The suspension is warmed to 20 °C, whereupon an intensely yellow reaction solution slowly develops (2 h). At −78 °C, yellow crystals deposit. The supernatant liquid is removed by capillary and the product washed with cold diethyl ether and dried under vacuum at −30 °C; yield 1.51 g (99%). Anal. Calcd for $C_{30}H_{66}P_4Pd_2$ (763.6): C, 47.19; H, 8.71; P, 16.23; Pd, 27.87. Found: C, 47.21; H, 8.83; P, 16.18; Pd, 27.74. Raman: 1370 cm^{-1} (μ-C≡C, bound). ^1H NMR (400 MHz, 27 °C): δ 5.75 (m, 2 H, μ-C_2H_2); δ 1.89, 1.93 (each 4 H, PCH and PCH′), 1.49 (8 H, PCH_aH_b), 1.18, 1.08, 1.03, 0.99 (each 12 H, CH_3; phosphane). ^{13}C NMR (75.5 MHz, −30 °C): δ 67.7 (m, 2 C, ^1J(CH) = 200 Hz, μ-C_2H_2); δ 26.1, 25.9 (each m, 4 C, PCH and PC′H), 21.1, 20.2, 19.4, 18.7 (each m, 4 C, CH_3), 22.7 (m, 4 C, PCH_2; phosphane). ^{31}P NMR (−30 °C): δ 59.9.

{(^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$)Pd}$_2$(μ-C$_2$D$_2$) (13a): synthesis as for **13** but with **11a**. IR (KBr): 1316 cm^{-1} (μ-C≡C, bound).

{(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd}$_2$(μ-C$_2$H$_2$) (14). Solutions of the ethyne complex **12** (451 mg, 1.00 mmol) and the ethene complex **10** (453 mg, 1.00 mmol) in diethyl ether (each 15 mL) are combined at 20 °C. Within 2 days light yellow needles crystallize. The supernatant liquid is removed by capillary and the product washed with diethyl ether and dried under vacuum; yield 725 mg (80%). Anal. Calcd for $C_{38}H_{82}P_4Pd_2$ (875.8): C, 52.12; H, 9.44; P, 14.15; Pd, 24.30. Found: C, 52.08; H, 9.54; P, 14.11; Pd, 24.21. IR (KBr) and Raman: 3065, 3024 cm^{-1} (≡C—H, bound), 1370 cm^{-1} (C≡C bound). ^1H NMR (400 MHz, 27 °C): δ 5.66 (m, 2 H, μ-C_2H_2); δ 1.67 (8 H, PCH_aH_b), 1.26, 1.21 (each 36 H, $C(CH_3)_3$ and $C'(CH_3)_3$; phosphane). ^{31}P NMR (27 °C): δ 80.0.

{(^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$)Pd}$_2$(μ-C$_2$D$_2$) (14a): synthesis as for **14** but with **12a**. IR (KBr) and Raman: 2325, 2255 cm^{-1} (≡C—D, μ-bound), 1320 cm^{-1} (C≡C, μ-bound).

Acknowledgment. We thank Dr. Klaus Seevogel for the IR and Raman studies and Dr. Richard Mynott for the NMR spectra.

Registry No. **1**, 138234-13-6; **2**, 138234-14-7; **3**, 138234-15-8; **4**, 138234-16-9; **5a**, 138234-17-0; **5b**, 138331-40-5; **6a**, 138234-18-1; **6b**, 138331-41-6; **7**, 138234-19-2; **8**, 138234-20-5; **9**, 138234-21-6; **10**, 138234-22-7; **11**, 138234-23-8; **11a**, 138234-24-9; **12**, 138234-25-0; **12a**, 138234-26-1; **13**, 138234-27-2; **13a**, 138234-28-3; **14**, 138234-29-4; **14a**, 138234-30-7; Pd(η^3-C_3H_5)$_2$, 12240-87-8; ^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr$_2$, 87532-69-2; ^{t}Bu$_2$PC$_2$H$_4$P^{t}Bu$_2$, 107783-62-0.

η^2-(C,O) Ketene Coordination at Nickel(0). Synthesis, Bonding, and Molecular Structure of (dtbpm)Ni[η^2-(C,O)-Ph_2C_2O][†]

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Received August 15, 1991

Qualitative electronic structure considerations and MO model calculations are presented, which predict η^2-(C,O) coordination to be preferred over η^2-(C,C) coordination for ketene complexes of P_2Ni^0 and P_2Pt^0 (d^{10}) bis(phosphane) metal fragments. The relative energetic preference for an η^2-(C,O)-bonding mode of ketenes is shown to increase with a decreasing P–M–P angle. Bis(di-*tert*-butylphosphino)methane (^{t}Bu$_2$PCH$_2$P^{t}Bu$_2$, dtbpm) is a tailor-made chelating bis(phosphane) ligand, which allows one to realize P–Ni–P angles below 80° within four-membered NiPCP chelate rings. Starting from the stilbene complex (dtbpm)Ni(η^2-*trans*-PhCH═CHPh) (**25**), the 14-electron intermediate [(dtbpm)Ni^0] could be generated and trapped by diphenylketene to yield the η^2-(C,O)-coordinated diphenylketene complex (dtbpm)Ni[η^2-(C,O)-Ph_2C_2O] (**30**), which has been characterized spectroscopically and by X-ray diffraction. Crystals of compound **30**·C_6D_6 ($C_{31}H_{48}OP_2Ni\cdot C_6D_6$) are monoclinic, space group $P2_1/n$, with $a = 11.957$ (2) Å, $b = 14.911$ (2) Å, $c = 20.111$ (2) Å, $\beta = 99.73$ (1)°, $V = 3534.0$ Å^3, and $Z = 4$. The molecular structure of **30** provides the first example of a nickel triad ketene complex, for which ketene to metal bonding has been established unequivocally. Its η^2-(C,O) geometry is in accord with EH model calculations for Ni and Pt, but it contrasts ab initio results for analogous platinum systems reported in the literature and may have interesting consequences for understanding reactivity patterns of d^{10}-ML_2 ketene complexes (M = Ni(0), Pd(0), Pt(0)).

Introduction

Transition-metal complexes with ketene ligands have found much attention in recent years, and their chemistry has been extensively reviewed by Geoffroy and Bassner.[1] To a large part the impetus to synthesize and to study transition-metal ketene complexes comes from the assumption that they might play an important role as model compounds for homogenous or heterogeneous Fischer–

[†] Dedicated to Prof. Wolfgang Beck on the occasion of his 60th birthday.

(1) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1.

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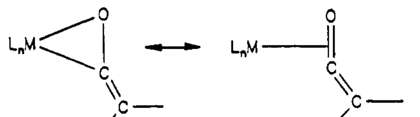
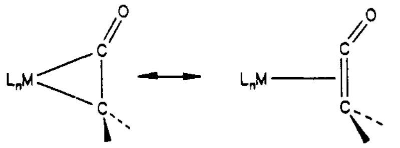
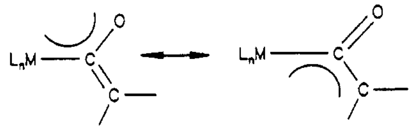
Tropsch type processes,[2a-h] i.e. in the field of stoichiometric or catalytic CO activation and reduction chemistry, involving C–C coupling or decoupling steps mediated by transition-metal centers. The coordination of ketenes to metals not only allows one to stabilize these often highly reactive and transient species within the ligand sphere of mono- or polynuclear organometallic complexes but also modifies their geometries, electronic structures, and thus their reactivity patterns as compared to the free organic molecules. A related area of active research, where ketene complexes may play the role of model compounds, is CO_2 fixation and functionalization.[2i-k] Ketenes have been shown to display a wide variety of different bonding modes toward metal fragments, depending upon the specific type and number of metal atoms, their spatial arrangement, oxidation state, and coligand environments. Even for mononuclear ketene complexes, three basic structural alternatives **1**–**3**, are possible and have been established experimentally.[3]



1 η^2-(C,O)



2 η^2-(C,C)

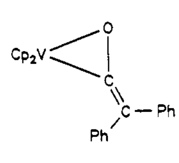


3 η^1-(C)

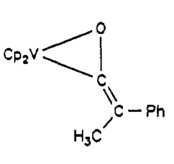
In this paper we report the synthesis and molecular structure determination of an unusual bis(phosphane) Ni(0) ketene complex which, for the first time, establishes η^2-(C,O) (type 1) ketene to metal bonding for a zerovalent d^{10} metal center. The results presented here for a tailor-made phosphane ligand environment at dicoordinated Ni(0) may be of general significance for the chemistry of d^{10}-ML_2 transition-metal ketene complexes of the nickel triad and shed some new light upon previous experimental and theoretical work in the literature.

Experimental and Theoretical Background

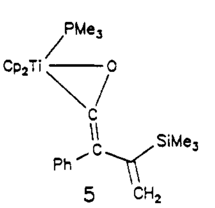
Let us first summarize briefly the known structural chemistry of ketene complexes, restricting the discussion to the mononuclear cases **1**–**3**. As expected, ketene complexes of early, very oxophilic transition metals all display η^2-(C,O) (metallaoxirane type) geometries **1** in their ground states. X-ray structure determinations have been reported for V^4 (**4a,b**), Ti^5 (**5**), and Zr^6 (**6a,b**). Coordination mode



4a



4b



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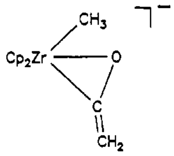
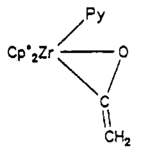


6a



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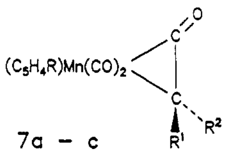
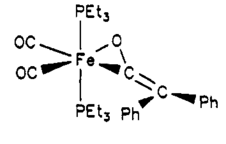


7a – c



a : R = H, $R^1 = R^2$ = Ph

b : R = Me, R^1, R^2 = $C_{13}H_8O$

c : R = Me, R^1, R^2 = $C_{14}H_{12}$

8

2, η^2-(C,C) (metallacyclopropanone type), has so far been studied by X-ray diffraction only for some structurally closely related ketene complexes of Mn^7 (**7a**–**c**).[8] Structure **3**, of η^1-(C) type, better viewed as a metal-substituted enolate,[9] is included here just for completeness, because it can be formally regarded as resulting from **1** by M–O bond heterolysis (oxygen decoordination) and because such structures may therefore play a role in the course of reactions of species **1**.

Especially in the context of ketene complex reactivity, it is of some importance to outline experimentally and to understand theoretically those factors which determine the preference of the ambident ketene π-system to adopt either η^2-(C,O) (**1**) or η^2-(C,C) (**2**) coordination. Despite the seemingly clear-cut cases of η^2-(C,O)-bound early-transition-metal ketene complexes (V, Ti, Zr, etc.), the specific choice for other metals is by no means easily predictable.

The manganese structures of **7a**–**c** for instance are contrasted by the molecular structure of the diphenyl-

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(2) (a) Ichikawa, M.; Sekizawa, K.; Shikakura, K.; Kawai, M. *J. Mol. Catal.* **1981**, *11*, 167. (b) Takeuchi, A.; Kratzer, J. R. *J. Phys. Chem.* **1982**, *86*, 2438. (c) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (d) Bell, A. T. *Catal. Rev.* **1981**, *23*, 203. (e) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (f) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (g) Blyholder, G.; Emmet, P. H. *J. Phys. Chem.* **1960**, *64*, 470. (h) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (i) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (j) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57. (k) Dötz, K. H. *Nachr. Chem., Tech. Lab.* **1990**, *38*, 1388.

(3) Other coordination modes of ketenes or derivatives thereof in di- and oligonuclear complexes can be found in ref 1, p 16 ff.

(4) (a) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173. (b) Galante, J. M.; Bruno, J. W.; Hazin, P. N.; Folting, K.; Huffmann, J. C. *Organometallics* **1988**, *7*, 1066.

(5) Meinhart, J. O.; Santarsiero, B. D.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 3318.

(6) (a) Ho, S. C. H.; Straus, D. A.; Armantrout, J.; Schaefer, W. P.; Grubbs, R. H. *J. Am. Chem. Soc.* **1984**, *106*, 2210. (b) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, 108, 2086.

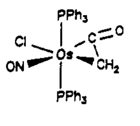
(7) (a) Redhouse, A. D.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 615. (b) Herrmann, W. A.; Plank, J.; Ziegler, M.; Weidenhammer, K. *J. Am. Chem. Soc.* **1979**, *101*, 3133. (c) Herrmann, W. A.; Plank, J.; Kriechbaum, G. W.; Ziegler, J. L.; Pfisterer, H.; Atwood, J. L.; Rogers, R. D. *J. Organomet. Chem.* **1984**, *264*, 2327.

(8) We disregard here structures of mononuclear ketene complexes where, as in $(CO)_3Fe(Ph_2C_2O)$ (Bkouche-Waksman, I.; Ricci, J. S., Jr.; Koetzle, T. F.; Weichmann, J.; Herrmann, W. A. *Inorg. Chem.* **1985**, *24*, 1492), in $Cp(CO)(PMe_3)W[Me_2PC(Me)CO]$ (Kreissl, F. R.; Wolfgruber, M.; Sieber, W.; Ackermann, K. *J. Organomet. Chem.* **1983**, *252*, C39), or in various vinylketene complexes (for a literature collection see: Hofmann, P.; Hämmerle, M.; Unfried, G. *New. J. Chem.*, in press) additional functionalities of the ketene ligands (double bonds, arene rings, lone-pair-carrying atoms, etc.) are bound to the metal center. A collection of such systems may be also found in ref 1.

(9) (a) Aklogu, N.; Felkin, H.; Baird, G. W.; Davies, S. G.; Watts, O. *J. Organomet. Chem.* **1984**, *262*, 49. (b) Liebeskind, L. S.; Welker, M. E.; Goedken, V. *J. Am. Chem. Soc.* **1984**, *106*, 441. (c) See also ref 1, pp 116–118.

ketene complex **8**, very recently published by Berke et al.,[10] with an η^2-(C,O) ketene. From the literature available to us, the series **4–8** with an overall number of nine examples seems in fact to represent all such compounds, for which their η^2-(C,O) or η^2-(C,C) structures have been established by X-ray crystal structure determinations.

Of course a much larger number of ketene complexes has been synthesized and has been characterized spectroscopically. Without attention to those, which are simple analogues of **4–8**, the others do not give a consistent picture of the necessary prerequisites or limitations for η^2-(C,O) or η^2-(C,C) bonding. Different from **8**, Roper's isoelectronic Os complex **9**[11a] has been described as η^2-(C,C), just as Cutler's cationic system **10**.[11b,c] The cyclopentadienylidene ketene complex **11** of Re, made by the Casey group,[12] at variance with Mn compounds **7a–c**, is of the metallaoxirane η^2-(C,O) type, as are some Mo systems[13] like **12** and **13**.



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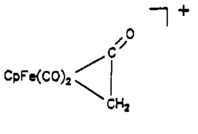

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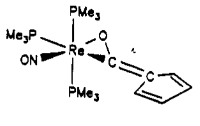

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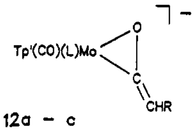
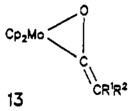


12a – c

a : L = CO, R = H
b : L = CO, R = CH3
c : L = P(OPh)3, R = CH3



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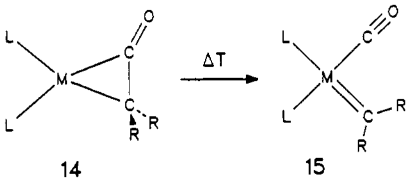
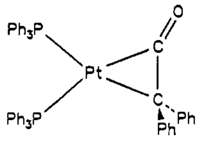
a : R1 = R2 = Ph
b : R1 = Ph, R2 = Et

Our own interest in transition-metal ketene complexes was raised by the chemistry reported in the literature for ketene complexes of d[10] metal centers of the nickel triad. Despite the immense number of alkene and alkyne complexes of Ni(0), Pd(0), and Pt(0), only a few ketene complexes of these metals are known (or have been postulated as intermediates), and none of them has been characterized by X-ray diffraction yet. This seems somewhat surprising, because it is this class of compounds which has been claimed recently to undergo a remarkable, facile η^2-(C,C) ketene cleavage process leading from **14** to **15** (M = Ni, Pt; vide infra), thus modeling an important elementary step of potential Fischer–Tropsch mechanisms.[14]



14 15

The first Pt(0) ketene complex, **16**, was synthesized by Beck and Schorpp[15] in 1973 and, on the basis of IR spectroscopy (ν_{CO} = 1742 cm^{-1}), was assigned as η^2-(C,C). In 1985, Miyashita[16] reported the preparation of **17** with unsubstituted ketene as ligand[17] and again an η^2-(C,C) coordination mode was deduced from IR and NMR data. The synthesis of **17** was claimed to occur by metal-mediated CH_2/CO coupling, i.e. the reverse of the **14** to **15** transformation.



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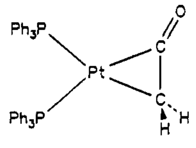

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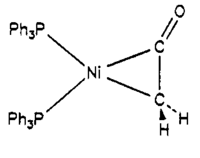

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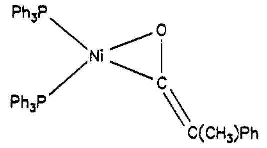

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Platinum, palladium, and nickel ketene complexes of η^2-(C,C) structure were also postulated as reactive intermediates in catalytic alkoxy- and aminocarbonylation reactions of geminal dibromoalkanes.[18] As to Ni(0) ketene complexes, Hoberg and Korff[19a] have described the synthesis of the Ni analogue of **16**, $(PPh_3)_2Ni(Ph_2C_2O)$, but its structure could not be elucidated. From spectroscopic data, η^2-(C,C) coordination in a mononuclear complex as in **16** could be definitely excluded. The structures of pyridine and bipyridine derivatives of this Ni(0) diphenylketene complex, prepared by the same authors, are also unknown, but again η^2-(C,C) geometries are inconsistent with the spectroscopic data. These findings strongly contrast later reports by Miyashita,[20] who has published the synthesis and isolation of **18**. Unlike in the diphenylketene case, NMR data and an IR band at 1750 cm^{-1} were interpreted as clear-cut proof of an η^2-(C,C)-bonding situation, just as in **16** and **17**. If, however, unsubstituted ketene was replaced by methylphenylketene, as in later work by Miyashita,[21] the structure of the resulting $(PPh_3)_2$Ni(methylphenylketene) complex revealed spectral and chemical properties which were again different both from Hoberg's diphenylketene case and from **18**, suggesting strongly that **19**, an η^2-(C,O)-bound molecule, is formed in this case. Quite obviously there exists a need to take a closer look upon these systems.

Apart from the available and confusing experimental background, a second challenge to deal with ketene complexes of the Ni triad came from a recent theoretical paper

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(10) Birk, R.; Berke, H.; Hund, H.-U.; Huttner, G.; Zsolnai, L.; Dahlenburg, L.; Behrens, U.; Sielisch, T. *J. Organomet. Chem.* **1989**, *327*, 397.

(11) (a) Gallop, M. A.; Roper, W. R. *Adv. Organomet. Chem.* **1986**, *25*, 121. (b) Bodnar, T. W.; Cutler, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5926. (c) Bodnar, T. W.; Crawford, E. J.; Cutler, A. R. *Organometallics* **1986**, *5*, 947.

(12) (a) Casey, C. P.; O'Connor, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 2919. (b) Casey, C. P.; O'Connor, J. M.; Haller, K. J. *J. Am. Chem. Soc.* **1985**, *107*, 3172.

(13) (a) Rusik, C. A.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 4652. (b) Reference 4b. (c) Okuda, J.; Herberich, G. E. *J. Organomet. Chem.* **1987**, *320*, C35.

(14) (a) Keim, W. *Catalysis in C_1 Chemistry*; D. Reidel: Dordrecht, 1983 (see also references therein). (b) See also ref 2a–h.

(15) Schorpp, K.; Beck, W. *Z. Naturforsch.* **1973**, *28B*, 738.

(16) Miyashita, A.; Shitara, H.; Nohira, H. *Organometallics* **1985**, *4*, 1468.

(17) Reference 16 also describes square-planar and octahedral Pt(II) ketene complexes $Cl_2Pt(H_2C_2O)$ and $Cl_2Pt(PMe_2Ph)_2(H_2C_2O)$ with η^2-*(C,C)* bonding assignment.

(18) Miyashita, A.; Kihara, T.; Nomura, K.; Nohira, H. *Chem. Lett.* **1986**, 1607. In this paper the clean isolation also of the Pd ketene complex $L_2Pd(H_2C_2O)$, analogous to the Pt and Ni cases is mentioned. None of the two references cited contains any palladium chemistry, however. To the best of our knowledge, no ketene complex of Pd(0) is known yet.

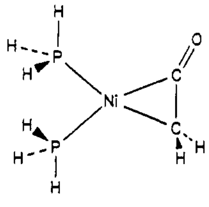
(19) (a) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *152*, 255. (b) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *152*, C39.

(20) Miyashita, A.; Shitara, H.; Nohira, H. *J. Chem. Soc., Chem. Commun.* **1985**, 850.

(21) Sugai, R.; Miyashita, A.; Nohira, H. *Chem. Lett.* **1988**, *1403*.

of the Morokuma group[22] which, by means of ab initio MO model calculations, studied the **14** to **15** transformation (M = Pt, L = PH_3). Both on the RHF and on the MP2 level, the η^2-(C,C)-bonding mode of $(PH_3)_2Pt(H_2C_2O)$ was found to be more stable than the η^2-(C,O) structure after complete geometry optimization with gradient techniques. The RHF (MP2) energy preference for the η^2-(C,C) form is 5.7 (7.3) kcal mol^{-1}, the barrier height calculated for the C–C bond breaking step of the ketene within the Pt coordination sphere to yield the square-planar methylene carbonyl complex **15** (M = Pt, L = PH_3) amounts to 37 kcal mol^{-1}, and the reaction is endothermic by 28 kcal mol^{-1}. At the same time, the computed dissociation barrier of ketene from the $(PH_3)_2Pt$ metal fragment is reported to be only 19 kcal mol^{-1} and the ketene to Pt binding energy is only 13 kcal mol^{-1}. These numbers would seem to rule out definitely the metal-centered **14** to **15** transformation as a realistic possibility, at variance with Miyashita's interpretation, because ketene dissociation would win out by far. These discrepancies remain unresolved in Morokuma's theoretical study. Obviously, they either must mean that Miyashita's experimental observations and perhaps even structural assignments need to be reinterpreted or that the ab initio numbers are not reliable and cannot reproduce the experimental facts. In the latter case, some doubt would be also cast upon the computed relative energies of the η^2-(C,C) and η^2-(C,O) forms of the platinum system.

This was in fact suggested by earlier extended Hückel[23] calculations performed by us[24] for **20** and **21** (M = Ni, Pt) with model geometries and only partial geometry optimization.



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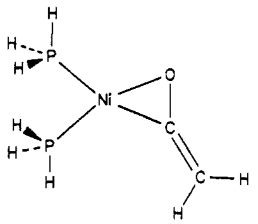
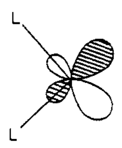
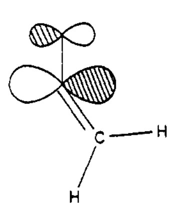


21

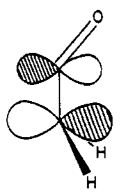
For all reasonable structural assumptions, EH calculations had predicted **21** with η^2-(C,O) bonding to be more stable for both metals. Although EH results should be generally taken with great care in an absolute numerical sense, we noted that the computed preference for **21** was in accord with simple qualitative and perturbation considerations of dominant bonding interactions between a bent d^{10}-ML_2 metal fragment and a ketene unit. From an analysis of frontier MO interactions, the lower energy of **21** could be traced back mainly to the better back-bonding from the metal fragment's familiar high-lying b_2-type HOMO,[25] sketched in **22**, into the π^*_{CO} orbital **23** of the ketene carbonyl group, which is the LUMO of the ligand system. It is much lower in energy and thus closer to the metal HOMO b_2 than the π^*_{CC} orbital **24** of a H_2C_2O fragment, both for a linear ground-state ketene and for ketene geometries which are bent appropriately to be prepared for η^2-(C,O) or η^2-(C,C) bonding to $(H_3P)_2M$ as indicated in **23** and **24**.



22 (b_2)



23 (π^*_{CO})

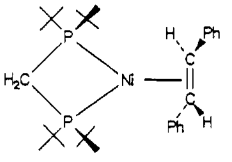


24 (π^*_{CC})

From a simple perturbational point of view, the smaller frontier orbital energy separation between MO **22** of a d^{10}-ML_2 unit and MO **23** of the η^2-(C,O) ketene ligand causes better metal to ligand back-bonding, stronger charge transfer, and an energetic preference for **21** vs **20**.

As it is well documented[25,26] that the MO energy of the b_2 HOMO of a bent d^{10}-ML_2 unit becomes drastically destabilized if the L–M–L angle is decreased, it seemed reasonable to assume that small P–M–P angles of $(R_3P)_2Ni$ or $(R_3P)_2Pt$ 14-electron fragments should make the b_2–π^*_{CO} interaction of η^2-(C,O) structures even more dominant, compared to the b_2–π^*_{CC} back-donation in their η^2-(C,C) isomers. Given the choice, a d^{10}-ML_2 unit with a very high lying b_2 HOMO and strong π-back-bonding capability ought to opt for a better π-acceptor as its ligand, and ketenes ought to be better π-acceptors in their η^2-(C,O)-bonding mode.[27]

We have recently shown[28] that P–M–P angles even below 75° can be enforced for bis(phosphane) ML_2 fragments by the unusual ligand bis(di-*tert*-butylphosphino)methane,[29] $^t\mathrm{Bu_2PCH_2P^tBu_2}$ (dtbpm). Due to its special properties detailed elsewhere,[30] dtbpm not only allows one to synthesize stable square-planar d^8-complexes of Ni(II), Pd(II), and Pt(II) with four-membered MPCP chelate rings but also renders unusual stability to d^{10}-complexes (dtbpm)M(L) (M = Ni, Pd, Pt; L = olefins, alkynes, etc.). Despite their predicted instability[25b] the dtbpm ligand even makes 14-electron intermediates [(dtbpm)M] (M = Ni, Pd, Pt) with extremely squeezed P–M–P angles of ca. 75° (105° less than the linear d^{10}-ML_2 equilibrium geometry) accessible as reactive intermediates, if suitable precursors are utilized to generate them. The olefin complex **25**, prepared by us recently and characterized by X-ray crystallography, allows us to generate [(dtbpm)Ni] in solution and to study the chemistry of this highly strained



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[22] Nakamura, S.; Morokuma, K. *Organometallics* **1988**, *7*, 1904.

[23] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1379.

[24] Schmidt, H. R. Dissertation, Technical University of Munich, 1988.

[25] (a) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 364 ff. (b) Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 7482.

[26] Hofmann, P.; Heiss, H.; Müller, G. *Z. Naturforsch.* **1987**, *42B*, 395 and references therein.

[27] The reverse effect, i.e. L–M–L angle decrease following stronger π-acceptor capability of ligands, has been observed and interpreted theoretically along these lines: Yoshida, T.; Tatsumi, K.; Otsuka, S. *Pure Appl. Chem.* **1980**, *52*, 713.

[28] (a) Hofmann, P.; Perez-Moya, L. A.; Krause, M. E.; Kumberger, O.; Müller, G. *Z. Naturforsch.* **1990**, *45B*, 897. (b) Hofmann, P.; Heiss, H.; Neiteler, P.; Müller, G.; Lachmann, J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 880. (c) Hofmann, P. In *Organometallics in Organic Synthesis*; de Meijere, A.; tom Dieck, H., Eds.; Springer: Berlin, Heidelberg, 1987. (d) See also ref 26.

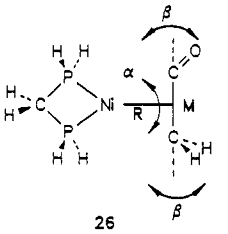
[29] Karsch, H. H. *Z. Naturforsch.* **1983**, *38B*, 1027.

[30] Detailed in ref 10a of ref 28b.

d^{10}-ML_2 system. On the basis of the qualitative electronic structure arguments above, **25** seemed to be a suitable starting material to attempt the synthesis of an η^2-(C,O) ketene complex of nickel in order to unequivocally establish its bonding mode and to prove or disprove the validity of contradicting experimental assignments and theoretical predictions.

MO Model Calculations

To test our hypothesis of a preference for η^2-(C,O) vs η^2-(C,C) bonding for small P–M–P angles, we have computed the relative energies for models of the two possible (dtbpm)Ni systems which might result from **25**, namely for **26** and **27**, using the diphosphinomethane ligand



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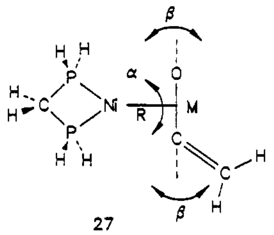

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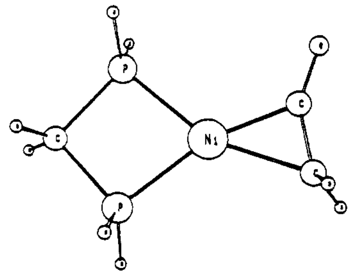

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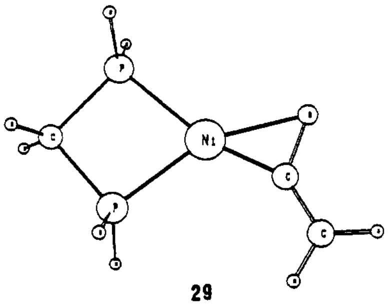

29

(dhpm) with a P–Ni–P angle of 79° in the (dhpm)Ni fragment.[31] For a fixed ketene ligand geometry (see Experimental Section), prepared for η^2-(C,O) and η^2-(C,C) bonding, we optimized the relative position of each ketene unit by varying the two angles α and β. α is the angle between the vector from Ni to the C–C (**26**) or C–O (**27**) midpoint M and the x-axis, β is the in-plane pivoting angle of the C–C and C–O bonds around their center M. This choice of parameters allows the unsymmetrical ligand to find the best relative in-plane position and to adopt simultaneously inequivalent Ni–C and Ni–O bond lengths for a given Ni to ligand distance R ($\alpha = \beta = 0°$ corresponds to a symmetrical position of the ketene with two equidistant Ni–C bonds for **26** and identical Ni–C and Ni–O bonds in **27**, respectively.) For all reasonable values of R the η^2-(C,O)-bonding mode is found at lower energy, if two-dimensional energy surfaces $E = E(\alpha, \beta)$ are calculated. The two minimum-energy structures, which are reached if we start out from symmetrical geometries ($\alpha = \beta = 0°$) with Ni–C = 2.0 Å in **26** and with Ni–C = Ni–O = 1.87 Å in **27**,[32] are displayed in **28** and **29**.

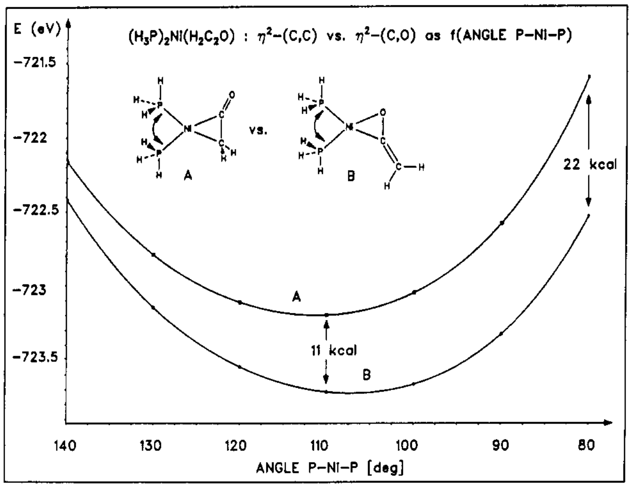

Figure 1. Total energy of $(H_3P)_2Ni[\eta^2$-(*C*,*C*)-$H_2C_2O]$ (upper curve) and $(H_3P)_2Ni[\eta^2$-(*C*,*O*)-$H_2C_2O]$ (lower curve) as a function of the P–Ni–P angle between 140 and 80°.

The η^2-(C,O) isomer is more stable by as much as 22 kcal, and the unsymmetrical disposition of H_2C_2O in **28**, with a shorter Ni–C bond to the carbonyl carbon (sp^2), follows qualitative expectations and experimental findings. The more stable η^2-(C,O) system **29**, in agreement with Morokuma's ab initio results for $(H_3P)_2Pt(H_2C_2O)$, has a Ni–C bond length shorter than Ni–O, with a rather weak and ionic Ni–O bond (charge on O, −1.140). Again, it should be emphasized that the energies and structures for **28** and **29** ought to be viewed as a qualitative trend rather than in an absolute sense, but the relevant point is that the energy ordering with η^2-(C,O) lower than η^2-(C,C) persists for all meaningful values of R[33] and that the same results are found as well for (dhpm)Pt as the metal fragment.[34] When we compute the relative energies for η^2-(C,O) and η^2-(C,C) structures as a function of the P–Ni–P or P–Pt–P angle in $(H_3P)_2Ni(H_2C_2O)$ and $(H_3P)Pt(H_2C_2O)$ in order to check the qualitative conclusion of an increasing energetic preference for the η^2-(C,O)-bonding mode with decreasing P–M–P angle, the results also corroborate the expectations. Figure 1 gives the total energy of $(H_3P)_2Ni[\eta^2$-(*C*,*C*)-$H_2C_2O]$ (upper curve) and $(H_3P)_2Ni[\eta^2$-(*C*,*O*)-$H_2C_2O]$ (lower curve) as a function of the P–Ni–P angle between 140 and 80°.

η^2-(C,O) bonding leads to lower energies throughout, but the energy difference grows from 6 kcal at P–Ni–P = 140° to 22 kcal at P–Ni–P = 80°, a value identical to the energy difference found for the chelate models **26** and **27**. The reader may also note that the minima of both curves do not coincide. Compared to the η^2-(C,C) case (112°) the best P–Ni–P angle for the η^2-(C,O)-bonding mode is smaller by some 10° (102°), again consistent with the stronger π-accepting power of the C,O-coordinated ketene ligand, to which the metal fragment adapts by increasing its own π-donor capacity through a smaller P–M–P angle and a higher lying HOMO. From a theoretical point of view, binding a ketene to the (dtbpm)Ni chelate ring system of

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[31] Taken from the X-ray structure of (dtbpm)Ni(η^2-*trans*-PhCH=CHPh) (**25**); see ref 28a.

[32] Structural data adapted from the various η^2-(*C*,*O*) and η^2-(*C*,*C*) ketene complexes as well as from η^2-(*C*,*O*) ketone complexes of $(R_3P)_2Ni$ fragments, for which X-ray structure determinations have been reported in the literature.

[33] If, in addition to α and β, R is varied between 2.0 and 1.3 Å, EH calculations not unexpectedly give too short Ni–C and Ni–O bonds, but the higher stability of the η^2-(*C*,*O*) form persists throughout.

[34] Pt calculations: Hofmann, P.; Blumenthal, A. Unpublished results.

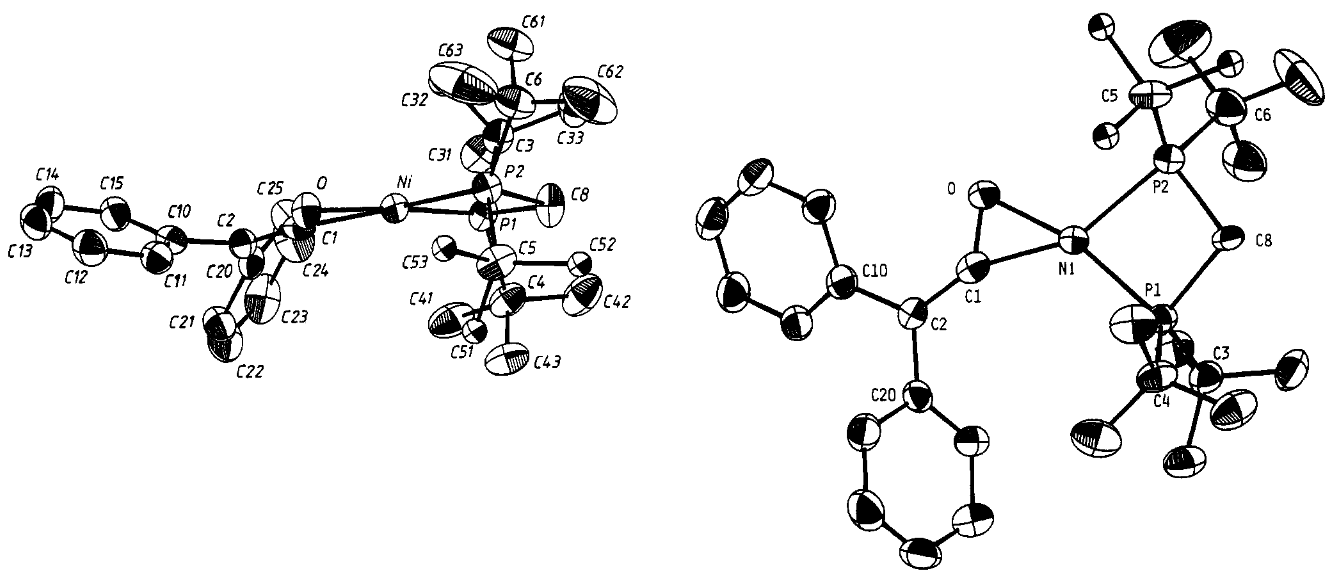
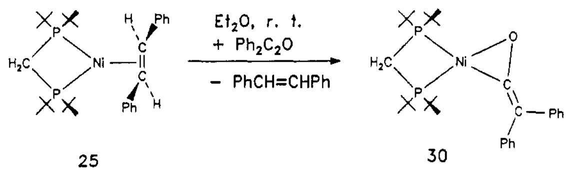


Figure 2. Perspective views of the molecular structure of **30** and the atomic-numbering scheme used (ORTEP, thermal ellipsoids at the 50% probability level). Only one of the possible positions of C51, C52, and C53 is shown. H atoms are omitted for clarity.

25 thus seemed to offer a good chance for reaching a stable η^2-(C,O) complex structure.

Synthesis of [η^2-Bis(di-*tert*-butylphosphino)methane][η^2-(*C*,*O*)-diphenylketene]nickel(0), (dtbpm)Ni[η^2-(*C*,*O*)-Ph_2C_2O] (30)

Assuming not only that the chelated (dtbpm)Ni fragment would offer favorable electronic prerequisites for η^2-(C,O) ketene coordination but also that the steric bulk around the metal would help to ensure a monomeric nature of a potential ketene complex, with just one ketene ligand binding to the Ni, we chose diphenylketene as a substrate for the [(dtbpm)Ni] fragment precursor **25**. This specific ketene not only is reasonably stable as a monomer but also allows a direct comparison to the majority of known ketene complexes, where diphenylketene was used as a ligand as well (Fe, Mn, Ti, Zr, V, Ni, Pt complexes, vide supra). When a solution of **25** in ether was allowed to react with an equimolar amount of diphenylketene at room temperature, a yellow-orange crystalline precipitate was formed, which could be isolated in around 55% yield and which, from spectroscopic data and elemental analysis was a 1:1 complex of a (dtbpm)Ni unit with diphenylketene (eq 1).



(1)

25 30

Interestingly, the η^2-(C,O) coordination mode of this extremely moisture-, air-, and temperature-sensitive material could be already deduced unequivocally from its ^1H NMR spectrum and (less safely) from its IR data. No IR band between 1700 and 2400 cm^{-1} is found; a band at 1643 cm^{-1} is indicative of a C=C double bond, but in comparison to other systems does not prove[1] a C,O-bound ketene. The aromatic region of the ^1H NMR spectrum displays a splitting pattern, which clearly establishes the presence of two *inequivalent* phenyl rings in **30**. Shifted to lower field (by ca. 0.3 and 0.7 ppm) with respect to the rest of the aromatic signals (six protons), there are two well-separated unique multiplets, each corresponding to two phenyl protons. Only the η^2-(C,O) ligand coordination of **30** allows for this pattern; an η^2-(C,C) structure would have two *equivalent* phenyl rings by symmetry, with ortho, meta, and para protons appearing in a 4:4:2 (2:2:1) ratio.[35] Only the C,O-coordinated structure is also consistent with a total of eight peaks between 121 and 138 ppm for the phenyl carbons in the ^{13}C spectrum, again indicating two *inequivalent* C_6H_5 rings (two different ipso carbons, two different pairs of ortho and meta carbons, two different para carbons). Although not very probable for steric reasons (as revealed by molecular models and by molecular graphics studies[36]), a dimer or oligomer structure (e.g. analogous to early-transition-metal cases) could not be excluded from analytical and spectroscopic data; a solution molecular weight determination was not reliably possible due to the high sensitivity of **30**. We therefore undertook an X-ray structure determination to ascertain the molecular geometry of this ketene complex.

Crystal and Molecular Structure of 30

Yellow-orange single crystals of **30**, suitable for an X-ray structure determination, were obtained from a C_6D_6 solution used for NMR spectroscopy by slow evaporation of the solvent from an NMR tube at room temperature within a glovebox under argon. Crystal data for **30** are given in Table I.

30 crystallizes with four discrete molecules per unit cell and cocrystallizes with one C_6D_6 molecule per monomer. As there are no relevant contacts between the solvent and the complex in the solid state, we will only discuss the Ni complex as such. The molecular geometry of **30** is shown in Figure 2 (hydrogens omitted for clarity) for two orientations of the molecule.

The positional and thermal parameters of the non-hydrogen atoms are listed in Table II, and selected bond distances, bond angles, and torsion angles in Table III. The diphenylketene ligand is η^2-(C,O)-coordinated to Ni. The ligand environment of the metal can either be described as trigonal planar (taking the η^2-(C,O)-bonded ketene unit as one ligand) or as distorted square planar.

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[35] This intensity ratio assumes free phenyl rotation at room temperature, as found in all related systems.

[36] Using, e.g., ALCHEMY II molecular modeling software, Tripos Ass., Inc.

Table I. Crystal Structure Data of 30•C_6D_6 and Structure Determination Details

chem formula	$C_{31}H_{48}NiOP_2{\cdot}C_6D_6$
mol wt	641.50
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.957 (2)
b, Å	14.911 (2)
c, Å	20.111 (2)
β, deg	99.73 (1)
V, Å^3	3534.0
Z	4
cryst dimens, mm	0.20 × 0.28 × 0.60
d_{calcd}, g·cm^{-3}	1.206
μ(Mo Kα), cm^{-1}	6.65
F(000)	1368
T, °C	−50
radiation	Mo Kα
λ, Å	0.71069
scan type	ω
scan width, deg	0.9
hkl range	±13,16,20
no. of reflctns measd	7985
no. of unique reflctns	5537
R_{int}[a]	0.032
no. of reflctns obsd	4417
param ref	355
R[b]	0.058
R_w[c]	0.058
$\delta\rho_{fin}$ (max/min), e/Å	+0.61/−0.41

[a] $R_{int} = [\sum(N\sum_n w(\langle F\rangle - F)^2)/\sum((N-1)\sum_n wF^2)]^{1/2}$. [b] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $w = 1/w^2(F_o)$.

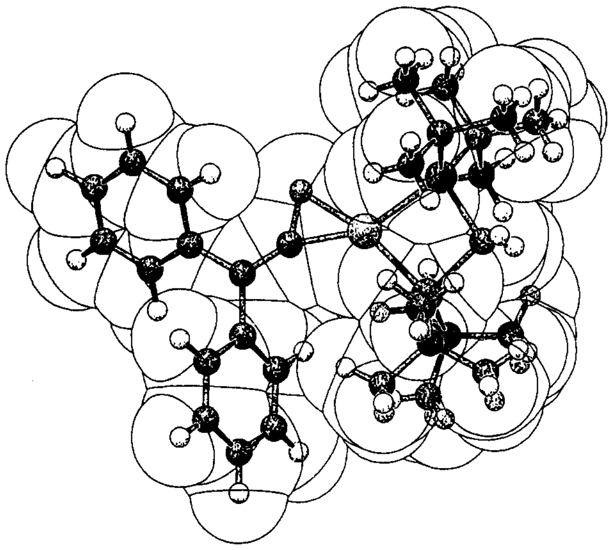

Figure 3. Space-filling representation of 30 (top view, hydrogens included) with ball and stick skeleton inserted for clarity (SCHAKAL).

The (dtbpm)Ni part of the complex displays some interesting features, especially when compared to the structural data of the stilbene complex 25 used as the starting material.[28a] The two Ni–P bonds (both 2.222 (1) Å in 25) are distinctly different. Whereas the one trans to the (sp^2-type) carbon atom of the Ni–C–O ring (2.267 (1) Å) is marginally longer than Ni–P of 25, in accord with the higher s-character of the metal-coordinated carbon in 30, the Ni–P distance trans to oxygen (2.180 (1) Å) is significantly shorter, reflecting the much smaller trans effect of the more ionic and polar Ni–O bond in 30. The P–Ni–P angle of 79° is identical to the one found for 25 and is somewhat larger than in (dtbpm)Pt compounds.[26,28b] The P–C distances within the NiPCP ring are equal and identical in both compounds within experimental error.

Table II. Final Fractional Coordinates of the Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters for 30

atom	x/a	y/b	z/c	U(eq), Å^2
Ni	0.24028 (5)	0.42665 (4)	0.21622 (3)	0.045
P1	0.3365 (1)	0.49396 (9)	0.30385 (6)	0.043
P2	0.3943 (1)	0.4739 (1)	0.17399 (6)	0.051
O	0.1311 (3)	0.3683 (2)	0.1544 (2)	0.051
C1	0.0937 (4)	0.3783 (3)	0.2109 (2)	0.055
C2	−0.0033 (4)	0.3534 (3)	0.2315 (2)	0.050
C8	0.4477 (4)	0.5344 (4)	0.2553 (2)	0.039
C10	−0.0880 (4)	0.2998 (3)	0.1873 (2)	0.060
C11	−0.1072 (4)	0.3098 (4)	0.1160 (3)	0.064
C12	−0.1815 (4)	0.2537 (4)	0.0750 (3)	0.075
C13	−0.2392 (4)	0.1867 (4)	0.1025 (3)	0.084
C14	−0.2217 (4)	0.1763 (4)	0.1718 (3)	0.071
C15	−0.1486 (4)	0.2312 (4)	0.2128 (3)	0.065
C20	−0.0231 (4)	0.3756 (4)	0.3010 (3)	0.051
C21	−0.1251 (4)	0.4172 (4)	0.3098 (3)	0.078
C22	−0.1464 (4)	0.4359 (5)	0.3732 (3)	0.098
C23	−0.0698 (5)	0.4173 (5)	0.4290 (3)	0.066
C24	0.0302 (5)	0.3759 (5)	0.4217 (3)	0.079
C25	0.0539 (4)	0.3567 (4)	0.3581 (3)	0.065
C3	0.4109 (4)	0.4182 (4)	0.3750 (2)	0.053
C31	0.3560 (4)	0.4216 (4)	0.4383 (2)	0.063
C32	0.3972 (4)	0.3218 (4)	0.3497 (3)	0.072
C33	0.5383 (4)	0.4405 (4)	0.3950 (3)	0.070
C4	0.2853 (4)	0.5992 (4)	0.3418 (3)	0.061
C41	0.1827 (5)	0.5784 (4)	0.3758 (3)	0.100
C42	0.3815 (5)	0.6453 (4)	0.3907 (3)	0.080
C43	0.2450 (5)	0.6632 (4)	0.2840 (3)	0.092
C5	0.3584 (4)	0.5602 (4)	0.1054 (2)	0.062
C6	0.5154 (4)	0.4026 (4)	0.1550 (3)	0.090
C61	0.5476 (5)	0.3369 (5)	0.2130 (3)	0.115
C62	0.6210 (5)	0.4550 (6)	0.1492 (4)	0.188
C63	0.4762 (6)	0.3480 (6)	0.0923 (4)	0.201
C70	−0.1887 (6)	0.7117 (5)	0.0548 (5)	0.128
C71	−0.1171 (7)	0.6577 (6)	0.0281 (4)	0.100
C72	−0.0577 (6)	0.5938 (6)	0.0668 (5)	0.149
C73	−0.0723 (7)	0.5859 (5)	0.1328 (5)	0.141
C74	−0.1455 (8)	0.6431 (7)	0.1576 (4)	0.116
C75	−0.2028 (6)	0.7052 (6)	0.1166 (6)	0.160
C51A	0.2628 (9)	0.6166 (9)	0.1199 (6)	0.036
C52A	0.472 (1)	0.622 (1)	0.0999 (7)	0.052
C53A	0.314 (1)	0.511 (1)	0.0376 (8)	0.065
C51B	0.268 (1)	0.504 (1)	0.0451 (8)	0.034
C52B	0.440 (1)	0.612 (1)	0.0762 (8)	0.037
C53B	0.280 (1)	0.639 (1)	0.1314 (8)	0.036
C51C	0.358 (1)	0.519 (1)	0.0343 (7)	0.027
C52C	0.230 (2)	0.590 (1)	0.111 (1)	0.059
C53C	0.440 (2)	0.644 (1)	0.117 (1)	0.063

The four-membered NiPCP ring is planar, its interplane angle with the NiCO nickelaoxirane ring is 5°. The sum of interligand angles at the nickel center of 359.9° shows planar metal tetracoordination. As already found for 25,[28a] one of the four *tert*-butyl groups is disordered (only one of three possible positions is shown in Figure 1). The disordered ^{t}Bu substituent belongs to the ^{t}Bu pair with less sterically crowded environment cis to the oxygen atom. The (dtbpm)Ni unit of 30, again similar to the structure of 25[28a] and of (dtbpm)$NiCl_2$,[28a,37] shows a remarkable local distortion and symmetry reduction toward C_2, caused by an inequivalent "bending back" of the *tert*-butyl groups at P1 and P2, away from the coordinated ketene. While angles Ni–P1–C3 and Ni–P2–C5 are 112.8 and 116.5°, respectively, the two other ^{t}Bu groups, also trans to each other, lean back with Ni–P1–C4 = 123.1° and Ni–P2–C6 = 126.9°, i.e. by around 10° more. This difference of the two Ni–P–$C_{^tBu}$ angles at each phosphorus, as indicated schematically in 31, increases from (dtbpm)$NiCl_2$ (ca. 6°)

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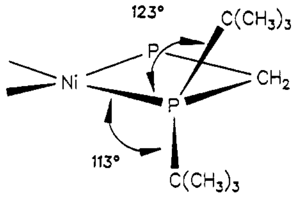
(37) (a) Krause, M. A. Diploma Thesis, Technical University of Munich, 1988. (b) Reber, G. Dissertation, Technical University of Munich, 1988.



31

via **30** (ca. 10°) to **25** (ca. 20°), indicating the increasingly severe steric interference of the bulky (dtbpm)Ni subunit with the additional ligands at Ni, shown in Figure 3 in a space-filling representation for **30**.

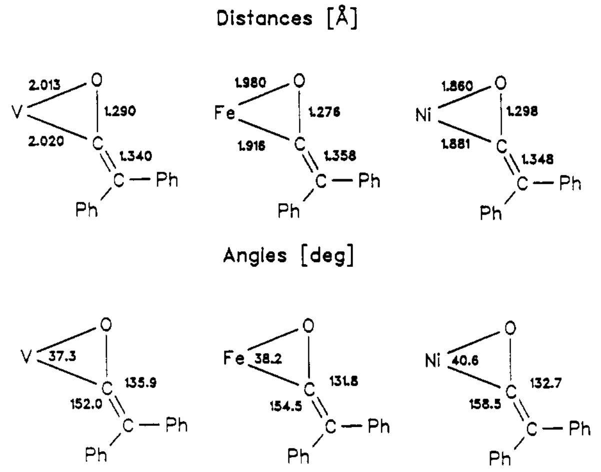
As we have not observed this C_2-type different bending back of two mutually trans *tert*-butyl groups in the molecular structures of (dtbpm)PdCl$_2$[37,38] and (dtbpm)PtCl$_2$,[26] there must be more intrinsic steric crowding (^{t}Bu/^{t}Bu repulsion of transannular and geminal type) within the overall more compact (dtbpm)Ni fragment with its smaller metal atom and thus shorter metal to ligand bonds. A structural comparison of the NiCO three-membered ring of **30** with those of the other (mononuclear) η^2-(C,O) complexes of diphenylketene,[39] **4a** and in particular **8**, is of interest. Relevant distances and angles are displayed in Scheme I.

In both Cp$_2$V(Ph$_2$C$_2$O) and (CO)$_2$(PEt$_3$)$_2$Fe(Ph$_2$C$_2$O) the metal–oxygen and metal–carbon bonds are longer than for **30**. In the case of vanadium, this is consistent with the larger atomic radius[40] (1.35 Å) of the early transition metal as compared to Ni and thus is not too conclusive for a comparison of the bonding capability of Cp$_2$V vs the (dtbpm)Ni fragment. There is also a distinct bond shortening toward O and C in the Ni compound compared to the Fe complex **8**, although the metal atomic radii are nearly identical (1.26 Å for Fe, 1.25 Å for Ni[40]). Moreover, opposite to the iron case, the metal to oxygen bond is slightly shorter in **30** than the corresponding metal to carbon distance, whereas the C–O bond length of the coordinated ketene is more elongated in the Ni system than for Fe, being practically identical to the vanadium compound and precisely as long as in the η^2-(C,O)-bound Cp$_2$Ti complex **5**. In the absence of any other η^2-(C,O) ketene structures at Ni, the NiCO ring of **30** can only be compared to those of three structurally characterized η^2-(C,O) complexes with keto ligands or to the single example with CO$_2$. Unlike for (PCy$_3$)$_2$Ni(η^2-CO$_2$)[41a] (shorter) and (PPh$_3$)$_2$Ni[η^2-(CF$_3$)$_2$CO][41b] (identical), the Ni–C distances are longer than in **30** in the two keto systems (Et$_3$P)$_2$Ni(η^2-Ph$_2$CO)[41c] and (PPh$_3$)$_2$Ni[η^2-(Et)PO(OMe)$_2$CO][41d], whereas all Ni–O bond lengths are comparable, although that of the CO$_2$ complex seems somewhat elongated.[42] The longer C–O bonds of η^2-coordinated keto compounds (1.33 Å average) compared to **30** or **8**, as well as longer Ni–C bonds and the differences to the CO$_2$ complex, are again consistent with the hybridization difference of the metal-bound carbon. The weak trans effect of the η^2-(C,O) oxygen is seen in all P$_2$Ni fragments of the η^2-(C,O) keto complexes. They all display a shortened Ni–P bond trans to the O atom as found in **30**.

Table III. Selected Interatomic Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for 30 with Estimated Standard Deviations

	Distances		
Ni–P1	2.180 (1)	Ni–P2	2.267 (1)
Ni–O	1.860 (3)	Ni–C1	1.881 (5)
P1–C8	1.878 (5)	P1–C3	1.920 (5)
P1–C4	1.891 (5)	P2–C8	1.881 (5)
P2–C5	1.883 (5)	P2–C6	1.887 (6)
O–C1	1.298 (6)	C1–C2	1.348 (7)
C2–C10	1.466 (6)	C2–C20	1.494 (7)
C10–C11	1.422 (7)	C10–C15	1.400 (7)
C11–C12	1.386 (7)	C12–C13	1.381 (8)
C13–C14	1.383 (8)	C14–C15	1.368 (7)
C20–C21	1.407 (7)	C20–C25	1.374 (6)
C21–C22	1.371 (9)	C22–C23	1.352 (8)
C23–C24	1.375 (9)	C24–C25	1.387 (8)
	Angles		
P1–Ni–P2	79.0 (1)	P1–Ni–O	166.1 (1)
P2–Ni–O	114.7 (1)	P1–Ni–C1	125.6 (2)
P2–Ni–C1	154.9 (2)	O–Ni–C1	40.6 (2)
Ni–P1–C8	92.9 (1)	Ni–P1–C3	112.8 (2)
Ni–P1–C4	123.1 (2)	C3–P1–C4	109.1 (2)
Ni–P2–C8	90.1 (2)	Ni–P2–C5	116.5 (2)
Ni–P2–C6	126.9 (2)	C5–P2–C6	108.9 (3)
Ni–O–C1	70.6 (2)	Ni–C1–O	68.8 (2)
O–C1–C2	132.7 (4)	C1–C2–C10	120.5 (4)
C1–C2–C20	120.4 (4)	P1–C8–P2	97.6 (2)
	Torsion Angles		
Ni–P1–C8–P2	−5.7	O–Ni–P2–C8	172.7
P1–Ni–C1–O	178.7	P2–Ni–O–C1	−174.5
P2–Ni–C1–O	11.7	P1–Ni–O–C1	−4.4
Ni–O–C1–C2	−178.3	O–C1–C2–C20	180.0
O–C1–C2–C10	4.0		

Scheme I


Distances [Å]

Angles [deg]

The exo double bond C=CPh$_2$ of the nickelaoxirane shows no unusual features, both phenyl rings are twisted out of plane with dihedral angles of 51 and 33°, respectively. The more twisted, less conjugated one, cis to the Ni atom and in closer proximity to the ^{t}Bu groups at P1, has the longer C2–C$_{ipso}$ (C20) bond. The exo carbon C2 shows precise trigonal environment. The three-membered NiCO ring of **30** is not symmetrically disposed with respect to the P–Ni–P angle of the (dtbpm)Ni fragment, it is pivoted toward the oxygen side and toward P2, making P1–Ni–C1 = 125.6° and P2–Ni–O = 114.7°. We attribute this asymmetric location of the ketene ligand in **30** to the steric repulsion between the phenyl cis to Ni and the ^{t}Bu

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[38] The interesting molecular structural comparison of the three systems (dtbpm)NiCl$_2$, (dtbpm)PdCl$_2$, and (dtbpm)PtCl$_2$ will be published separately: Hofmann, P.; Krause, M. A.; Reber, G.; Müller, G., in preparation.

[39] Di- or oligomeric, anionic and other η^2-(*C,O*) complexes of Ph$_2$C$_2$O seem less useful for a direct comparison to **30**; we therefore restrict our discussion to **4a** and **8**.

[40] Shriver, D. F.; Atkins, P. W.; Langford, C. H. *Inorganic Chemistry*; Oxford University Press: Oxford, U.K., 1990; p 26.

[41] (a) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636. (b) Countryman, R.; Penfold, B. R. *J. Cryst. Mol. Struct.* **1972**, *2*, 281. (c) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311. (d) Nakazawa, H.; Nosaka, H.; Kushi, Y.; Yoneda, H. *Organometallics* **1990**, *9*, 1958.

[42] It should be noted that the X-ray structure of the nickel CO$_2$ complex is not a high-precision structure.

substituents at P1 (viz. Figure 3). The ketene bending angle C1–C2–O lies in the expected range.

Overall the ketene to Ni coordination in **30** is much tighter than that to V or Fe in **4a** and **8**. We interpret this as a reflection of the pronounced back-bonding capability of the (dtbpm)Ni unit into the π^*_{CO} orbital of the ketene ligand, noted already previously for **25**.[28a] In a sense, the dtbpm-enforced geometrical phosphane arrangement and the strong donor character of this bis(phosphane) seem to make the late-transition-metal center (d^{10}) structurally more similar to more electropositive, early transition metals in, e.g., Cp_2V (d^3) or Cp_2Ti, Cp_2Zr, etc. (d^2) fragments than to the d^8-FeL_4 unit of **8**. This is indeed also reflected in the chemistry of ketene complexes of (dtbpm)Pt, where the metal is even less oxophilic than nickel. This will be reported elsewhere.[43]

Conclusions

From qualitative MO arguments and EH model calculations, η^2-(C,O) bonding of a ketene ligand in bis(phosphane) Ni(0) complexes is suggested to be preferred over η^2-(C,C) coordination. With simple theoretical guidelines which predict increasing relative stability of η^2-(C,O) over η^2-(C,C) complexation with decreasing P–M–P angles for d^{10}-ML_2 bis(phosphane) fragments of the nickel triad, the ketene complex (dtbpm)Ni[η^2-(*C*,*O*)-Ph_2C_2O] (**30**) has been synthesized and its molecular structure has been determined. For the tailor made diphosphinomethane ligand dtbpm employed here, the d^{10}-P_2Ni fragment (dtbpm)Ni not only coordinates the diphenylketene at the carbonyl group but also seems to provide electronic and bonding properties which ressemble those of early-transition-metal fragments with a low d electron count rather than those of phosphane-substituted metal centers at the right end of the transition-metal block. Contrasting earlier ab intitio results by Morokuma et al.,[22] our experimental results for **30** as well as related model calculations and prelimary data from (dtbpm)Pt ketene chemistry[43] seem to suggest η^2-(C,O) ground state structures for related Pt(0) phosphane complexes as well. It is clear, however, that the energy difference between η^2-(C,O) and η^2-(C,C) bonding of ketenes at d^{10}-ML_2 fragments is relatively small. A deliberate choice of either coordination mode should thus be possible by rational ligand design, and potential rearrangement pathways between the two coordination modes might become interesting. The synthesis of **30** makes desirable a structure determination of the $(PPh_3)_2M(CH_2{=}C{=}O)$ (M = Ni, Pt) complexes reported by Miyashita[16,18,20] and strongly recommends a careful reconsideration of mechanistic assumptions based upon the assignment of η^2-(C,C) ketene coordination at P_2Ni and P_2Pt units.

The structure determination for **30** also sheds new light upon Hoberg's earlier nickel results,[19a] which excluded η^2-(C,C) type diphenylketene complexes without allowing the determination of the real structures of the probably oligomeric or polymeric $(PPh_3)_2Ni(Ph_2C_2O)$. An η^2-(C,O) geometry of **19**, as postulated on the basis of spectroscopic data, seems reasonable in light of the molecular geometry of **30**. At nitrogen-ligated (pyridine, TMEDA) Ni(0), diphenylketene could be dimerized to a product, which suggests η^2-(C,O) coordination of the first ketene.[19b] Although the IR spectrum of Beck's compound $(Ph_3P)_2Pt(Ph_2C_2O)$ (**16**) seems to point toward an η^2-(C,C) structure, a true structural proof for an η^2-(C,C) ketene complex of the nickel triad remains still to be seen. The synthesis and structure determination of $(PCy_3)_2Ni(Ph_2C_2O)$, where the P–Ni–P angle cannot become small due to the large cone angle of PCy_3, would be an interesting challenge in comparison to the diphosphinomethane ligand chosen here.

The η^2-(C,O) ground-state geometry of **30** also may bear some significance with respect to the reaction chemistry of CO_2 and other heterocumulenes at Ni(0), Pd(0), or Pt(0) centers with phosphane coligands,[43,44] and the related reactivity of the stereoelectronically unusual bis(phosphane) fragments [(dtbpm)Ni], [(dtbpm)Pd], and [(dtbpm)Pt] is currently under investigation in our laboratory.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry and oxygen-free argon in a glovebox (Braun, Model MB 150) or with standard Schlenk, septum/cannula, or vacuum-line techniques, removing traces of oxygen and water from commercially available argon in the latter cases by passage through columns with activated BASF copper catalyst and molecular sieves. Glassware was oven-dried at 140 °C prior to use. Diethyl ether was dried over sodium benzophenone ketyl; benzene and C_6D_6 were dried over sodium metal. All solvents were distilled under argon immediately before use. The olefin complex (dtbpm)Ni(η^2-*trans*-PhCH=CHPh) (**25**) was synthesized as reported earlier.[28a] Diphenylketene was prepared by literature procedures,[45] stored at −40 °C under argon, and freshly vacuum-distilled before use.

IR spectra were obtained on a Nicolet 5DX FT-IR spectrometer in KBr, and all NMR spectra on a JEOL-JNM-GX-270 spectrometer at room temperature in C_6D_6. ^1H and ^{13}C chemical shifts are reported in ppm downfield from TMS, using C_6D_5H of C_6D_6 (^1H NMR: 7.15 ppm relative to TMS) and C_6D_6 (^{13}C: NMR 128.0 ppm relative to TMS) signals as internal standards. ^{31}P NMR chemical shifts are given in ppm downfield from 85% H_3PO_4 as an external standard. Mass spectra were measured on a Varian MAT 311A mass spectrometer; elemental analyses were performed in the Microanalytical Laboratory of the institute. Melting points (uncorrected) were determined in a copper block using sealed glass capillaries.

[η^2-Bis(di-*tert*-butylphosphino)methane][η^2-(*C*,*O*)-diphenylketene]nickel(0), (dtbpm)Ni[η^2-(*C*,*O*)-Ph_2C_2O] (30). The *trans*-stilbene complex **25** (340 mg, 0.625 mmol) was dissolved in 30 mL of diethyl ether at room temperature. Using a dropping funnel or syringe/cannula techniques, an excess of diphenylketene (0.12 mL, 133 mg, 0.684 mmol), dissolved in 10 mL of diethyl ether, was slowly added to the orange-red solution. After ca. 1 h, a slight color change of the solution toward red-brown had occurred. The reaction mixture was stirred at room temperature overnight, during which time a yellow-orange crystalline precipitate had formed. After cooling to −20 °C for approximately 1 h, the product was collected on a fine frit, washed with cold diethyl ether, and dried in vacuo. Yield of **30**: 190 mg (54.5%). The compound is very air- and moisture-sensitive, especially when in solution. It decomposes rapidly above 40 °C. **30** could be recrystallized by slowly dissolving it in the minimum amount of diethyl ether at room temperature, filtering through a frit, and cooling the resulting solution to −78 °C. Yellow-orange crystals are obtained, mp 48–49 °C dec.

Spectroscopic data: IR (KBr) 3049, 3016, 2952, 2907, 2868, 1643 ($\nu_{C=C}$), 1599, 1566, 1483, 1450, 1437, 1392, 1366, 1238, 1180, 1167, 1096, 1070, 1025, 929, 773, 760, 742, 697, 664, 600, 581, 477 cm^{-1}; ^1H NMR δ 0.96 (d, 18 H, $^3J(P,H) = 13.2$ Hz, ^tBu), 1.17 (d, 18 H, $^3J(P,H) = 12.7$, ^tBu) [We have not investigated which ^tBu ^1H NMR resonance belongs to which ^tBu pair; it seems tempting to assign the higher field doublet at 0.96 ppm to the $P(^tBu)_2$ unit trans to oxygen, where the CH_3 groups on the average come close

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(43) Hofmann, P.; Unfried, G. Unpublished results. Presented at the IXth FECHEM Conference of Organometallic Chemistry, Heidelberg, 1991.

(44) The 14-electron fragment [(dtbpm)Pd] can be generated cleanly at room temperature from the *cis*-dialkyl complex precursor (dtbpm)-$Pd(CH_2{-}SiMe_3)_2$ by reductive elimination of $Me_3Si(CH_2)_2SiMe_3$. When this is done in the presence of diphenylketene, a stable, ketene-derived complex analogous to the Ni and Pt cases could not be isolated. Hofmann, P.; Krause, M. A. Unpublished work.

(45) Taylor, E. C.; McKillop, A.; Hawks, G. A. In *Organic Synthesis*; House, H. O.; Ed.; Wiley: New York, 1972; Vol. 52, p 36.

to the area above the face of the C20–C25 phenyl ring], 2.11 (t, 2 H, ^2J(P,H) = 6.8, CH_2), 7.0–7.3 (m, 6 H, C_6H_5), 7.63 (m, 2 H, C_6H_5), 8.04 (m, 2 H, C_6H_5); $^{13}C\{^1H\}$ NMR δ 30.34 (dd, J_1 = 8.5 Hz, J_2 = 10.5, CH_2), 30.67 (d, ^2J(P,C) = 6.4, CH_3), 30.87 (dd, J_1 = 7.3, J_2 = 1.0, CH_3), 34.27 (dd, J_1 = 10.2, J_2 = 4.4, CMe_3), 34.67 (dd, J_1 = 8.5, J_2 = 3.2, CMe_3), 121.57, 124.85, 125.87, 126.90, 128.87, 129.12, 133.91, 137.80 (eight different types of phenyl carbons for two inequivalent phenyl rings), 141.11 (dd, J_1 = 9.3, J_2 = 1.5, *C*O), 144.81 (d, J(P,C) = 3.4, *C*—C=O); $^{31}P\{^1H\}$ NMR δ 63.57 (d, ^2J(P,P) = 100.3 Hz), 38.49 (d, ^2J(P,P) = 100.3); mass spectrum (EI, 70 eV) (no molecular ion detectable) *m/e* 363 ($M^+ - Ph_2C_2O$, 1.65%), 332 ($Ph_2C{=}CPh_2$, 2.53), 249 ($M^+ - Ph_2C_2O - 2^tBu$, 1.88), 194 (Ph_2C_2O, 2.55), 192 ($M^+ - Ph_2C_2O - 3^tBu$, 2.75), 135 ($M^+ - Ph_2C_2O - 4^tBu$, 20.34), 57 (^tBu, 100).

Due to the high sensitivity of **30**, and also due to solvent cocrystallization (diethyl ether, benzene; viz. X-ray data below), an elemental analysis could only be obtained for **30**·C_6H_6. Anal. Calcd for $C_{37}H_{54}NiOP_2$ (635.48): C, 69.93; H, 8.56; Ni, 9.24; O, 2.52; P, 9.75. Found: C, 69.16; H, 8.39; Ni, 9.17; O, 3.08; P, 9.71.

X-ray Structure Determination and Refinement. Suitable single crystals of **30** were obtained from a C_6D_6 solution of an NMR sample by slow evaporation of the solvent from the NMR tube within a glovebox under argon. The crystals were sealed under an argon atmosphere at dry ice temperature into a Lindemann glass capillary. According to diffractometer measurements (Syntex P2$_1$) the compound crystallizes in the monoclinic space group $P2_1/n$. Reduced cell calculations (DELOS, LEPAGE) did not reveal any higher symmetry. The exact cell dimensions were obtained by a least-squares fit of the parameters of the orientation matrix to the setting angles of 15 centered high-order reflections from various parts of the reciprocal space. Crystal data and a summary of parameters pertinent to intensity data collection and structure refinement are given in Table I.

The integrated intensities of the reflections were measured on a computer-controlled four-cycle diffractometer (Syntex P2$_1$) using graphite-monochromated Mo Kα radiation. After Lorentz and polarization corrections, structure factors with $F_o < 4.0\ \sigma(F_o)$ were deemed "unobserved" and not used in all further calculations. No correction for absorption was required (low μ, well-shaped crystals, T_{max}/T_{min} = 1.087).

The structure was solved by direct methods (SHELXS 86) and completed by difference Fourier synthesis. All heavy atoms beside C51, C52, and C53 could be refined anisotropically. Relatively high anisotropic thermal parameters for some of the α-C atoms of the ^tBu groups strongly indicated static disorder of these atoms. The α-C atoms of the C5 ^tBu group were included in the refinement as a split model using three different positions for C51, C52, and C53 (sof A:B:C = 0.4:0.3:0.3). A total of 24 hydrogen atoms could be located; 21 were calculated at idealized geometrical positions (XANADU). H atoms of the C5 *tert*-butyl group were neglected. Final refinement was done by block-diagonal least squares with fixed H atoms (SHELX 76). Table II contains the final atomic coordinates of the non-H atoms. Table III summarizes important bond distances, bond angles, and torsional angles.

Molecular Orbital Calculations. The molecular orbital calculations were of the extended Hückel type.[23] A modified Wolfsberg–Helmholz formula[46] was employed for the calculation of H_{ij} matrix elements. The atomic parameters (wave functions, valence state ionization energies) for C, H, Ni,[47a] and P[47b] were taken from earlier work. The following geometric parameters[31,32] were used in the MO calculations. (dhpm)Ni fragments of **26** and **27**: overall C_{2v} symmetry; distances Ni–P = 2.20, P–C = 1.875, C–H = 1.10, P–H = 1.42 Å; angles P–Ni–P = 79, H–P–H = 110, H–C–H = 110°, hydrogen atoms on bisector planes of P–C–P and Ni–P–C angles.

η^2-(C,C) ketene ligand of **26**: C=O = 1.21, C—C = 1.42, C—H = 1.08 Å; O=C—C = 150, H—C—H = 110°, hydrogens on Ni—C—C bisector plane. NiCC ring: R = distance Ni–M = 1.869 Å, which makes both Ni–C = 1.87 Å for the symmetrical geometry with $\alpha = \beta = 0°$. η^2-(C,O) ketene ligand of **27**: C—O = 1.30, C=C = 1.35, C—H = 1.08 Å, O—C=C = 130, H—C—H = 120°. NiCO ring: R = distance Ni–M = 1.753 Å, which makes Ni–O = Ni–C = 1.87 Å for the symmetrical geometry with $\alpha = \beta = 0°$.

$(H_3P)_2Ni$(ketene) calculations for Figure 1: Ni(ketene) subunits as in **28** and **29**, corresponding to the $E = E(\alpha, \beta)$ minimum-energy structures of the dhpm systems **26** and **27**. $(H_3P)_2Ni$ fragment: C_{2v} symmetry, Ni–P = 2.2, P–H = 1.42 Å; PH_3 ligands tetrahedral. For hydrogen orientations, see **20** and **21**.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for their support of this work. We also gratefully acknowledge generous support from the BASF AG, and we thank Mrs. Annette Blumenthal for performing MO model calculations of related platinum systems in the course of undergraduate research work in our group,[34] as well as H. R. Schmidt for some related earlier $(H_3P)_2Ni(H_2C_2O)$ calculations.[24]

Supplementary Material Available: Complete tables of atomic and thermal parameters, bond distances, bond angles, and torsion angles for **30** (9 pages); a listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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[47] (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) See ref 26.