$_5$); Ir (on KBr pellet; cm^{-1}) 3494 (w), 3351 (m), 3283 (m), 2204 (s), 1643 (br), 1392 (w), 1366 (br), 1340 (w), 1262 (w), 1108 (br), 1054 (br), 808 (w), 716 (w), 516 (w); mass spectrum, m/e (relative intensity) 230 (M^+, 48). Anal. Calcd. for $C_9CoH_7N_4$: C, 47.00; H, 3.00. Found : C, 46.48; H, 2.82.

Acknowledgment. The Present Studies were partially Supported by the Basic Science Research Institute Program, Ministry of Education, 1994, Project No. 3426.

Reference

1. (a) Jonas, K.; Kruger, C. *Angew. Chem.* **1980**, *92*, 513. (b) Jonas, K. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 716.
2. Uhm, J. K.; Lee, H.; Byun, S. I.; Park, Y. B.; Kwak, Y. W.; Kim, T. J. *J. Kor. Chem. Soc.* **1991**, *35*, 410.
3. Bonneman, H. *Angew. Chem.* **1985**, *97*, 264.
4. Lee, W. S.; Lee, H.; Byun, S. I.; Park, Y. B.; Lee, K.; Uhm, J. K. *J. Kor. Chem. Soc.* **1992**, *36*, 305.
5. Herberich, G. E.; Hebner, B.; Beswetherick, S.; Howard, J. A. K.; Woodward, P. *J. Organomet. Chem.* **1980**, *192*, 421.
6. Heck, R. F. *Inorg. Chem.* **1968**, Vol. 7, No. 8, 1513.
7. Buffon, R.; Leconte, M.; Choplin, A.; Basset, J. *J. Chem. Soc., Chem. Commu.* **1993**, 361.
8. Espinet, P.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton trans.* **1979**, 1542.
9. Warren, L. *Inorg. Chem.* **1977**, *16*, 2814.
10. Leung, W. H.; Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2051.
11. Alobaidi, N.; McWhinnie, S. L. W.; Hamor, T. A.; Jonas, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 3299.
12. Redshaw, C.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1992**, 555.
13. Anillo, A.; Barrio, C.; Garcia-Granda, S.; Obeso-Rosete, R. *J. Chem. Soc., Dalton Trans.* **1993**, 1125.
14. Balch, A. L.; Holm, R. H. *J. Am. Chem. Soc* **1966**, *88*, 5201.
15. Paek, C.; Ko, J.; Uhm, J. K. *Bull. Kor. Chem. Soc.* Submitted for Publication.
16. Joh, T.; Hagihara, N.; Murahashi, S. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 661.
17. Michelman, R. I.; Bergman, R. C.; Andersen, R. A. *Organometallics*, **1993**, *12*, 2741.
18. Abd-El-Aziz, A. S.; Epp, K. M.; de Denus, C. R.; Fisher-Smith, G. *Organometallics*, **1994**, *13*, 2299.
19. (a) Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1436. (b) Saillard, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006.
20. Maroney, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1984**, *106*, 4144.

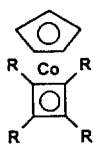
Reaction of $CpCo(C_2H_4)_2$ with Diphenylacetylene

Jae-Kook Uhm*, Hee-Won An, Chinkap Chung,
and Hong-Rak Kim†

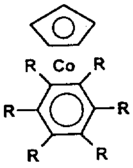
Department of Chemistry, Keimyung University,
Taegu 704-701, Korea
†*Department of Chemical Industry,*
Andong Technical Junior College, Andong 760-010, Korea

Received August 10, 1994

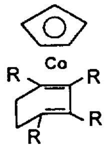
Since the first preparation of π-complexes of cyclobutadiene containing transition metals such as Ni, or Fe, the actual existence of cyclobutadiene fragment at room temperature has been reported.[1-2] 1,2,3,4-Tetraalkyl cyclobutadiene-cobalt complexes were prepared by the reaction of (η^5-cyclopentadienyl)di(carbonyl)cobalt[3] with dialkylacetylene in 1978.[4-5] Recently, (η^5-cyclopentadienyl)bis(ethylene)cobalt(Jonas reagent)[6] has been used for introducing (η^5-cyclopentadienyl)cobalt(CpCo)-moiety in the complex, CpCoL (L; 4π-electron donor ligand). Jonas reagent reacts with dialkylacetylene to give complexes [I], [II], [III] and [IV].[7]



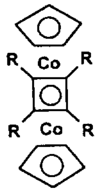
[I]



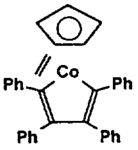
[II]



[III]



[IV]



[V]

In this paper we would describe the reaction and coordination chemistry of Jonas reagent with diphenylacetylene. A new complex, (η^5-cyclopentadienyl)ethylene(2,3,4,5-tetraphenyl cobaltacyclo-2,4-pentadiene)[V] was obtained in 77.4 % yield as a single product.[8] It is suggested that two molecules of diphenylacetylene are attacking cobalt metal of Jonas reagent to replace one of the two ethylene molecule in the reagent leaving an intermediate which has one molecule of ethylene and two molecules of diphenylacetylene.[7] This intermediate is expected to be unstable because it has 20 valence electrons (VE). Further rearrangement by dimerization of two diphenylacetylene molecules gave more stable complex [V] with 18 VE. The NMR spectrum of complex[V] showed that δ-values of ethylene in Jonas reagent shifted from 2.38, and 0.59 ppm to 2.43, and 1.50 ppm respectively, and that was due to the ring current effect of neighboring phenyl ring. Among the protons of four phenyl groups attached in the complex[V], those of the phenyl ring near ethylene molecule showed at 7.38 ppm and the other protons of the remaining three phenyl rings appeared broadly at 7.08 ppm. Molecular ion peak of complex[V] in mass spectrum was observed at m/e 508, and m/e 480 peak resulted from the elimination of ethylene from the complex[V].

We also found that the complex[V] was further decomposed during the chromatographic separation. Dark red crystalline complex[V] was dissolved in petroleum ether and separated as two bands on a silicagel column (2×15 cm). The

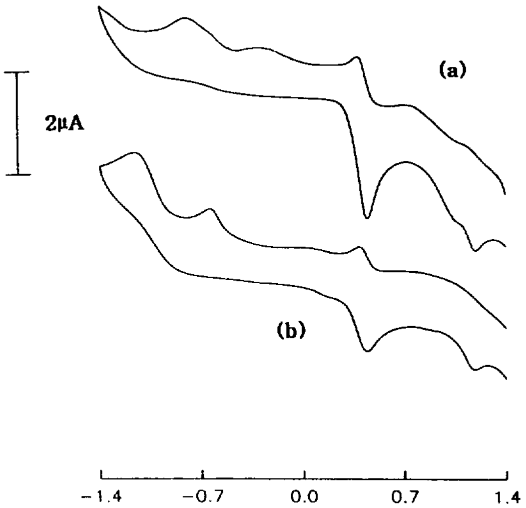
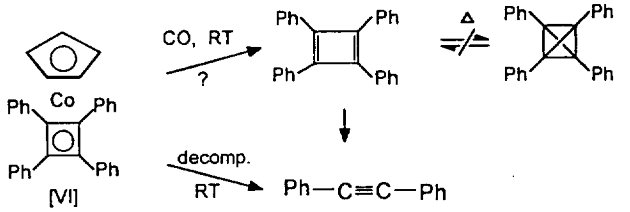


Figure 1. Cyclic voltammogram for complex[V] (a) and complex[VI] (b) with a platinum disc electrode in 0.1 M (n-Butyl)$_4$NPF$_6$/CH$_2$Cl$_2$ and a scan rate of 100 mV/s.

first band eluted with petroleum ether was identified to be the complex[V] (yield 48%). The second band eluted with tetrahydrofuran was orange red, and identified as complex [VI], (η^5-cyclopentadienyl)(η^4-1,2,3,4-tetraphenyl cyclobutadiene)cobalt[9] (yield 52%). It appeared that the elimination of one molecular ethylene from complex[V] on a silicagel column resulted in an unstable intermediate with 16 VE. This intermediate which was also appeared in the mass-spectrum of complex[V] rearranged to give a relatively stable complex[VI]. Complex[VI] was further decomposed to diphenyl acetylene after leaving at room temperature for two weeks.



It was previously reported that 1,2,3,4-tetra-*tert*-butyl cyclobutadiene rearranged to 1,2,3,4-tetra-*tert*-butyl tetrahedrane.[10] Since the complex[VI] has similar ligand 1,2,3,4-tetraphenyl cyclobutadiene, we expected to produce 1,2,3,4-tetraphenyl tetrahedrane *via* isolated 1,2,3,4-tetra-phenyl cyclobutadiene. We reacted complex[VI] with carbon monoxide at room temperature to exchange the ligands. We could not isolate either 1,2,3,4-tetra-phenyl cyclobutadiene nor 1,2,3,4-tetra-phenyl tetrahedrane. Instead, the final product was diphenyl acetylene. Exact meaning of this difference is not clear yet.

The oxidation and reduction characteristics of complexes [V] and [VI] were studied with electrochemistry and ESR.

The cyclic voltamograms of these complexes were shown in Figure 1.[11] Complexes[V] and [VI], both with 18 VE, were oxidized to monocations at 0.43 V and 0.45 V *vs.* Ag/AgCl respectively in reversible processes, and further oxidized to dications at 1.17 V and 1.20 V *vs.* Ag/AgCl respectively in irreversible processes. However, no further reduction to negatively charged complexes were observed in this experiment.

For ESR measurement of complex[V] and [VI], a potassium mirror was produced in an ESR probe and the tetrahydrofuran solution of complex[V] or complex[VI] was brought at −60 ℃ in contact with the potassium. However, the paramagnetic radical anions of these complexes were not observed. It means that the complex[V] and [VI] would not be reduced in this condition. This result is consistent with the absence of electrochemical reduction of complexes [V] and [VI] in cyclic voltametry.

In coclusion, the reaction of Jonas reagent with diphenylacetylene gave a new complex, (η^5-cyclopentadienyl)ethylene (2,3,4,5-tetra-phenyl cobaltacyclo-2,4-pentadiene), which was further decomposed to (η^5-cyclopentadienyl)(η^4-1,2,3,4-tetraphenyl cyclobutadiene)cobalt. Both complexes would not be easily reduced.

References

1. (a) Criegee, R.; Schröder, G. *Ann.* **1959**, *623*, 1. (b) Criegee, R.; Schröder, G. *Angew. Chem.* **1959**, *71*, 70.
2. (a) Emerson, G. F.; Walts, L.; Pettit, R. *J. Am. Chem. Soc.* **1969**, *87*, 131. (b) Maitlis, P. M. *Adv. Organomet. Chem.* **1966**, *4*, 95. (c) Belly, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343. (d) Pettit, R. *J. Organomet. Chem.* **1975**, *100*, 205.
3. Fischer, E. O.; Jira, R. *Z. Naturforsch. Teil B.* **1953**, *8*, 327.
4. Callot, M. J.; Schäffer, E. *J. Organomet. Chem.* **1978**, *145*, 91.
5. Weise, M. C.; Gordon, G. C.; Geochken, V. C. *J. Am. Chem. Soc.* **1979**, *101*, 857.
6. (a) Jonas, K.; Krüger, C. *Angew. Chem.* **1980**, *92*, 513. (b) Jonas, K. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 716.
7. (a) Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem.* **1983**, *95*, 729. (b) Kölle, U.; Fuss, B. *Chem. Ber.* **1986**, *119*, 116. (c) Uhm, J. K.; Park, Y. B.; Byun, S. I.; Lee, M.; Kwak, Y. W.; Kim, T. J. *J. Kor. Chem. Soc.* **1991**, *35*, 410. (d) Uhm, J. K.; Lee, W. S.; Kim, S. B.; Cha, J. S.; Lee, H. S.; Lee, D. H.; Kim, H. S.; Sim, S. C. *J. Kor. Chem. Soc.* **1993**, *37*, 832. (e) Rosenblum, M.; North, S.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239.
8. In a 100 m*l* Schlenk tube filled with Ar gas, Jonas reagent (1 g, 5.5 mmol) and diphenyl acetylene (2 g, 11.4 mmol) were dissolved in toluene (40 m*l*) at room temperature. After 120 h, the product was separated by column chromatography (SiO$_2$, 2×15 cm). Yield 77.4% (2.2 g, 4.3 mmol); mp. 175.7 ℃ ; ^{1}H NMR (C$_6$D$_6$) δ 1.5 (d, 2H, $^3J=9.6$ Hz), 2.43 (d, 2H, $^3J=9.6$ Hz), 4.70 (s, 5H), 7.08 (m, 15H), 7.38 (s, 5H); MS m/e [relative intensity] 508 (M$^+$, 42), 480 [(M-C$_2$H$_4$)$^+$, 20], 441 [(M-CpH$_2$)$^+$, 57], 189 [(CpCoCp)$^+$, 19], 149 [(CpCoC$_2$H)$^+$, 76], 124 [(CpCo)$^+$, 18], 65 [Cp$^+$, 29], 59 [Co$^+$, 49]; Anal. found (calcd. for C$_{35}$H$_{29}$Co): C, 83.2 (82.7); H, 5.8 (5.8).
9. mp. 189 ℃ ; ^{1}H NMR (C$_6$D$_6$) δ 4.68 (s, 5H), 7.09 (m, 20H);

MSm/e[relativeintensity]480[M^+,1.3],440[$(M\text{-}C_4H_4)^+$, 100], 124 [$CpCo^+$, 40.9], 77 [Ph^+, 24.6], 65 [Cp^+, 8.8], 59 [Co^+, 16.4]; Anal. found (calcd. for $C_{33}H_{25}Co$): C, 82.5 (82.5); H, 5.7 (5.3).

10. (a) Maier, G.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552. (b) Irngaitinger, H.; Riegler, N.; Malsch, K.-D.; Schneider, K.-A.; Maier, G. *Anew. Chem.* **1980**, *92*, 214.
11. Cyclic voltammograms were measured at room temperature in CH_2Cl_2 with $(n\text{-Butyl})_4N^+PF_6^-$ as a conducting salt. Working electrode, platimum disc; auxiliary electrode, platinum wire; reference electrode, Ag/AgCl.

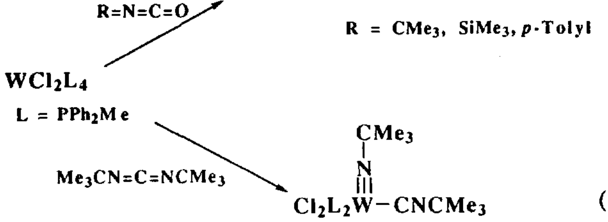
Molecular Structure of W(N^{t}Bu)(CO)(PPh$_2$Me)$_2$Cl$_2$

Geon-Soo Jung, June-Ho Jung, and Soon W. Lee*

Department of Chemistry, Sung Kyun Kwan University, Suwon, Kyung-Ki 440-746, Korea

Received July 2, 1994

Since the first nitrene complexes, OsO_3 (NR), were reported in 1959, transition-metal nitrene (or imido) complexes have received continuous interest.[1] For instance, high valent imido complexes can activate C-H bonds of several compounds.[2] Recently, Mayer's group reported that heterocumulenes such as isocyanates and carbodiimides react with $WCl_2(PPh_2Me)_4$ under mild conditions to form imido-carbonyl and imido-isonitrile complexes, respectively (Eq. 1).[3] These reactions were remarkable in that a formal double bond is cleaved to form a divalent and a neutral ligand. Very recently, Bergman and his workers reported an insertion of CO into an Ir≡N bond in $Cp^*Ir(\equiv N^tBu)(Cp^*=C_5(CH_3)_5)$, which is the first carbonylation of a terminal imido ligand to give an isocyanate complex.[4] The results of above studies prompted us to investigate the possibility of insertion reactions of CO into other terminal metal nitrene centers. We set out insertion reactions of carbon monoxide into W≡NR bonds. We report here the molecular structure of *trans, cis*-$W(PPh_2Me)_2Cl_2(N^tBu)(CO)$.



(1)

Experimental

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under an argon atmosphere. Carbonylation reactions have been performed in a 60 mL of quartz pressure vessel (Kontes). CO (99.9%) was purchased from Union Gas Co. and used as received. Trimethylphosphine (PMe_3; $Me=CH_3$, 1 M in toluene) and trimethylphosphite ($P(OMe)_3$) were purchased from Aldrich Co. and used as received. The title complex, **I**, was prepared by the literature method.[2]

Table 1. Crystallographic data and summary of data collection and structure refinement

formula	$C_{31}H_{35}NOP_2Cl_2W$	F (000)	1496
fw	754.29	no. of unique data	2511
crystal system	monoclinic		
space group	$P2_1$	no. of reflns used, I>2 σ (I)	2503
a, Å	10.731 (2)		
b, Å	21.371 (5)	no. of params	258
c, Å	13.851 (3)	Z	4
β, deg	90.40 (2)	scan range	$3<2\theta<50°$
V, Å^3	3716 (1)	scan type	ω-2θ
d_{calc}, g cm^{-3}	1.577	GOF on F^2	1.048
μ, mm^{-1}	3.930	R	0.0428
Max. in Δρ (e A^{3-})	0.60	wR_2[a]	0.0956

[a] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

X-ray Structure. All X-ray data were collected with use of an Enraf-Noinus CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with $16<2\theta<27°$. Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. The intensity data were empirically corrected with Ψ-scan data. All calculations were carried out on the personal computer with use of the SHELXS-86,[5] SHELXL-93[6] programs.

A brown crystal, shaped as a plate, of approximate dimensions 0.15×0.38×0.42 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences, $0k0$ ($k=2n+1$), indicated two possible space groups: of $P2_1$ and $P2_1/m$.. A statistical analysis of intensities of reflections suggested a noncentrosymmetric space group and the structure converged only in the space group $P2_1$. The structure was solved by the heavy atom methods. The W, Cl, and P atoms were refined anisotropically. The phenyl groups were treated as isotropic rigid groups. All hydrogen atoms were positioned geometrically and refined using a riding model. Final atomic positional parameters for non-hydrogen atoms are shown in Table 2 and the selected bond distances and bond angles are shown in Table 3; anisotropic thermal parameters, hydrogen atom coordinates, full bond distances and bond angles, and tables of observed and calculated structure factors are available as supplementary materials.

Results and Discussions

There are two crystallographically independent molecules